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**Production of Isopropyl Alcohol by Hydration of Propylene in a
Catalytic Distillation Column**

by

Yan Xu



A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirements for the degree of **Master of Science**
in
Chemical Engineering

Department of Chemical and Materials Engineering

Edmonton, Alberta

Spring 2002

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Production of Isopropyl Alcohol by Hydration of Propylene in a Catalytic Distillation Column** submitted by **Yan Xu** in partial fulfillment of the requirements for the degree of **Master of Science** in Chemical Engineering.

Abstract

Catalytic distillation technology was studied for the production of isopropyl alcohol (IPA) by hydration of propylene as an economical alternative of the traditional process. Key design parameters of the catalytic distillation column were determined using a commercial simulation program, AspenPlus™. The calculations were based on equilibrium-stage model for the distillation sections and equilibrium-reaction model for the catalytic sections. At optimum conditions, high purity IPA (99.9 *mol%*) was produced as a liquid product from the catalytic distillation column with dual catalyst beds at 2 MPa. Kinetics of Propylene direct hydration on Amberlyst 38 was experimentally measured. Reaction rate equations were found to follow Eley-Rideal model. Reaction rate based simulation of the process with the optimum configuration was conducted. The diameter of the column was 5.5 m, while the height of upper catalyst bed was 0.8 m and the height of lower catalyst bed was 2.1m.

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CHAPTER 1

INTRODUCTION

1.1 Isopropyl Alcohol Production

Isopropyl alcohol (IPA) has been called the first modern synthetic petrochemical. With physical characteristics compatible with those of alcohol, water, and hydrocarbons, IPA is a versatile and inexpensive solvent used widely in the chemical and cosmetics industries. Unlike ethanol, IPA is subject to few government regulations, and no special taxes are levied on its consumption. IPA is used as feedstock for the manufacture of acetone and other compounds, and is used widely as an antiseptic and disinfectant for home, hospital, and industry applications (Hancock, 1973; Kroschwitz, 1991).

In terms of production volume, IPA is about the fourth largest chemical. Total 1993 U.S. nameplate capacity for isopropyl alcohol production was 8.48×10^5 metric tons. The total world capacity is about 2.0×10^9 metric tons. The 1995 U.S. prices were \$0.55/L (\$2.10/gal) for refined 91vol % and \$0.62/L (\$2.36/gal) for anhydrous alcohol, an increase from the \$0.18/L (\$0.70/gal) average price of 1977. The price of IPA is driven by the price of propylene, the primary feedstock, and by the price of ethyl alcohol, a competing solvent (Logsdon and Loke, 1993).

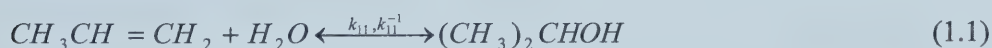
The future demand for IPA is expected either to remain flat or to grow slightly. Its main use as a chemical intermediate is growing, and this should offset the pressure on use as a solvent from tighter volatile organic chemicals (VOC) regulations.

The first industrial quantities of IPA were produced in 1920 in the world's first petrochemical plant, owned by Standard Oil Company (EXXON). To date, various methods for preparing IPA and various catalysts have been developed. The methods used most widely are direct hydration and indirect hydration of propylene (Kroschwitz, 1991). Both processes use propylene and water as raw materials. Other potential synthetic methods include fermentation of certain carbohydrates, oxidation of propane, hydrogenation of acetone, and hydrolysis of isopropyl acetate.

Indirect hydration is based on a two-stage process in which an ester is formed and then hydrolyzed to the corresponding alcohol. Reaction can be conducted through two operational models: two-step strong acid process; one-step weak acid process. Diisopropyl ether (DIPE) is the principal by-product.

Acid-catalyzed direct hydration of propylene to IPA is reversible and exothermic (Equation 1.1).

Hydration:



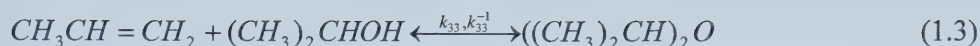
$$\Delta H = -50 \text{ kJ/mol } (-12 \text{ kcal/mol, } 298.15 \text{ K, } 1 \text{ atm})$$

DIPE is the principal by-product. The overall formation reaction of the ether may either be written as:



$$\Delta H = -15 \text{ kJ/mol } (-3.7 \text{ kcal/mol, } 298.15 \text{ K, } 1 \text{ atm})$$

or:



There are three propylene direct hydration processes in commercial operation: vapor-phase hydration over a fixed-bed catalyst (Kroschwitz, 1991); mixed vapor-liquid-phase hydration using strongly acidic proton-exchange resin catalyst (Neier and Woellner, 1973); and liquid-phase hydration in the presence of a homogeneous catalyst (Onoue *et al.*, 1978).

Economic comparisons of the indirect and direct hydration processes show a cost savings for use of the latter technology. The largest savings are in capital investment, processing and maintenance, all of which are necessitated by the troublesome sulfuric acid reconcentration of the indirect process. Greater corrosion and pollution problems are also associated with indirect hydration. However, drawbacks of direct hydration are its high energy usage and the need for highly concentrated propylene feedstock (Logsdon and Loke, 1993).

The required purity of IPA product depends on the intended application. The 91 vol% IPA azeotrope produced is sold as such or is dehydrated by azeotropic distillation to produce an anhydrous product. Minor impurities are removed and the odor of IPA is improved by use of either intense aqueous extractive distillation, or post-treatment by a fixed-bed absorption process using activated carbon, molecular sieves or metals and /or metal oxides of Group IB, VIB and VIII of the Periodic Table (Savini, 1978). Essence

grade IPA is produced by distillation of dehydrated IPA-water azeotrope in nonferrous equipment.

A typical conventional process scheme for direct hydration of propylene is shown in Figure 1.1. The principal difference between the direct and indirect processes is that much higher pressure is required for the direct hydration process. The slate and distribution of products and by-products from each process are similar, and systems for refining IPA are essentially the same.

1.2 Catalytic Distillation

Reactive distillation comprises the processes of catalytic reaction and multistage distillation carried out simultaneously in a single vessel. A reactive distillation column replaces the reactor and a series of distillation columns, thereby reducing the number of process vessels and materials transfer and control equipment required. Thus, capital costs are reduced (DeGarmo *et al.*, 1992).

The concept of reactive distillation is not new. It was first applied to esterification process using homogeneous catalysts in 1920's. The use of solid heterogeneous catalyst for reactive distillation is a more recent development, first described by Sennewald *et al.* (1971). The advantages of using solid catalysts over homogeneous catalysts are obvious: they are easy to separate from reaction mixtures, easy to handle and less waste. Solid catalysts also offer the potential for superior effectiveness and environmental integrity. However the column internals are more complicated when using solid catalysts.

Bubble-cap or sieve trays are common equipment used for homogenous reactive distillation processes. With high weirs, they provide the necessary liquid hold up and residence time needed for the reaction. Equipment for heterogeneous reactive distillation consists primarily of catalyst containing packing, which allows for simultaneous reaction and mass transfer between vapor and liquid phases. The heterogeneous catalyst acts as distillation packing as well as catalyst, therefore, heterogeneous reactive distillation is often termed as catalytic distillation (CD) to differentiate between the two processes (homogeneous and heterogeneous).

1.3 Applications of CD

CD is a viable option when the temperature and pressure of a process are such that the rate of reaction is sufficiently high under conditions for separation of products by distillation. The catalyst life must be long in order to avoid frequent start-up and shut-down. Equilibrium-limited reactions are excellent candidates for catalytic distillation; by continuously separating products from reactants while the reaction is in progress, the reaction can proceed to a much higher level of conversion than is attainable using a conventional process (Rock *et al.*, 1997; Shoemaker and Jones, 1987).

CD is potentially attractive whenever a liquid phase reaction must be carried out with a large excess of one reactant. Under such circumstances, conventional processes incur large recycling cost for the excess reactant. It may also be used for the separation of difficult systems. Podrebarac (1997) gave a comprehensive review of the various uses for CD prior to the end of 1996. A recent literature search revealed that a large

number of patents were granted in the last few years on the use of CD on a variety of chemical processes. These new CD processes are at various stages of development.

Rock *et al.* (1998) proposed a process for the improved sulfur removal from fluid catalytic cracking (FCC) gasoline via CD. Conducting hydrodesulfurization (HDS) to remove sulfur in a CD column offers the unique advantage to attain high sulfur conversion with minimal octane loss. This is due to the fact that the light olefins are concentrated at the top of the distillation column where the temperature is lower than the bottom of distillation column. This reduces the saturation of the light olefins and at the same time, light sulfur components could still be desulfurized at the top of the column. The higher molecular weight sulfur containing compounds undergo HDS at the bottom of the distillation column where the higher temperature facilitates the HDS process.

Another application of CD is the CD hydrogenation process, which combines fractionation together with hydrogenation. The CD process operates at substantially lower pressure than conventional hydrotreating processes due to the enhanced mass transfer between the vapor and liquid phases in the distillation process, which enables hydrogenation at high rates even at low hydrogen pressures.

A new CD application for the hydrogenation of benzene in reformate has been commercialized to produce gasoline that meets the benzene content specification (Rock, *et al.*, 1997). One application of this technology is the simultaneous processing of both

reformatted and light, straight-run gasoline in a single CD column. This option gives the refiner the capability to reduce benzene in gasoline while increasing the octane number.

CD was also applied to the remove of acetic acid from dilute acetic acid produced in many chemical and petrochemical industrial applications. In the CD column, methanol is introduced to react with acetic acid. The reaction product, methyl acetate, is removed from the top of the column and water is withdrawn from the bottom (Xu *et al.*, 1997).

Lee *et al.* (2000) used an isomerization reaction of 2-phenylethanol to p-ethylphenol in a catalytic distillation column to circumvent the azeotrope between p-ethylphenol and 2-phenylethanol. Placing sufficient reaction on only two trays in the top section of the column, the top operating line was shifted to below the 45° line. On lower nonreacting trays, the azeotrope was circumvented. It was found that the column temperature decreases from stages on the top of the column to those at the bottom of the column.

Currently, the largest commercial users of CD technology are fuel-ether producing units. A variety of ether, for example methyl tert-butyl ether (MTBE), tert-amyl methyl ether (TAME), ethyl tert-butyl ether (ETBE), tert-amyl ethyl ether (TAEE) and tert-hexyl ethyl ether (THEE), can be produced by reacting olefins having four, five, or six carbon atoms with methanol or ethanol (Zhang *et al.*, 1995; Subramaniam *et al.*, 1987; Rehfinger *et al.*, 1990; Rihko *et al.*, 1997; Podrebarac *et al.*, 1997; Ng *et al.*, 1999). MTBE is the first chemical commercially manufactured using CD technique.

1.4 Problem Definition

Direct hydration of propylene is the preferred process for production of IPA because it avoids some corrosion and environment problems encountered using indirect hydration processes. Improvements to the hydration process have been made in recent years on the operating conditions, catalyst, and extractive solvent (Bell *et al.*, 1996; Atkins, 1997; Brown *et al.*, 1996; Ramachandran *et al.*, 1996; Schmidt, 1984). However, current processes still require the use of complex distillation columns to recover IPA from the product stream, which leads to high energy usage. Separation of IPA from the azeotropic mixture is technically difficult and expensive.

The objective of this thesis research is to investigate a novel approach for the synthesis of IPA, catalytic distillation, as a simpler and less expensive alternative to conventional processes for production of IPA.

The research project consists of the following tasks:

1. Modeling of the catalytic distillation process. Initial simulation of the catalytic distillation was performed using a commercial simulation package – Aspen Plus. Impacts of key design parameters were examined systematically. An optimum configuration of the catalytic distillation column has been determined.

2. Reaction kinetic study. Kinetics of propylene hydration and IPA etherification were measured in a batch slurry reactor. The research includes: screening solid acid catalyst; eliminating internal and external mass transfer effects; studying effects of

temperature and reactant concentration on reaction rates; and deriving kinetic rate equations.

3. Design of CD column. A CD column for IPA production was sized and column configuration was determined by incorporating the reaction kinetics with the optimal simulation results.

1.5 Application of CD to Production of IPA

Propylene hydration to IPA is an excellent candidate for application of CD technology for the following reasons:

1. Direct hydration of propylene is an equilibrium-limited reaction (Equations 1.1-1.3).

2. Hydration takes place in the liquid phase; catalyst pellets remain completely wetted.

3. The reaction occurs at a temperature and pressure equivalent to the boiling point of the liquid product; thus distillation and reaction can be carried out simultaneously in the same column.

4. Hydration is exothermic; the heat of reaction provides a portion of energy required for the separation of the reaction mixture by distillation.

5. Durable heterogeneous hydration catalysts with suitable physical properties are commercially available (Kuo and Chen, 1999; Sonnemans, 1993; Odioso *et al.*, 1961).

6. In a CD hydration process, water will be continuously consumed by fresh propylene, and an IPA-rich stream will be continuously produced. Hence, equilibrium

limitations will be overcome, and the product stream will have a higher IPA content than product streams from conventional processes.

A major advantage of catalytic distillation over conventional fixed-bed reactors is the reduction in capital investment (Ng and Rempel, 1999; Podrebarac and Ng, 1997; Rock *et al.*, 1997). In addition, operating costs for production of IPA are reduced, as there is essentially no need to cool or heat the reactor. We will show that other benefits accrue from use of CD technique, including substantially complete consumption of water and improved selectivity to IPA. Safety and catalyst performance are also enhanced by use of CD technology, as the risk of formation of hot spots is lower in a CD system than in a conventional vapor phase hydration reactor.

1.6 Nomenclature

ΔH heat of reaction

1.7 Literature Cited

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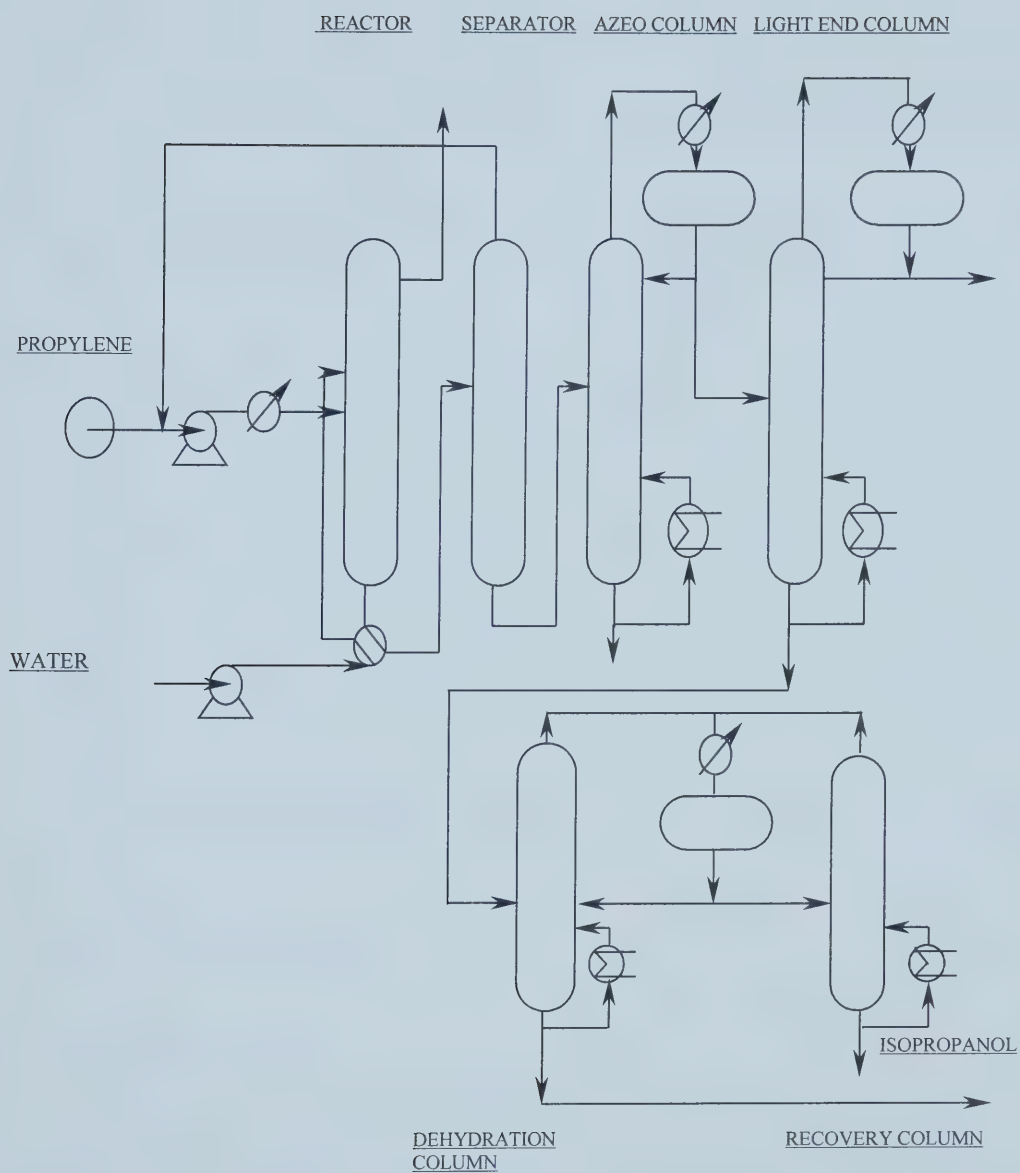


Figure 1.1 Flow diagram of Tokyoyama isopropyl alcohol process

CHAPTER 2

SIMULATION OF A CD PROCESS FOR IPA PRODUCTION

Simulation has become an essential component of catalytic distillation process design, and is even more important for CD process design than for design of conventional reactor/distillation systems. The interaction between simultaneous reaction and distillation processes increases the complexity of CD systems compared with systems comprising conventional reactors followed by distillation systems. Modeling methods are of even greater importance when there is no available satisfactory shortcut or empirical methods for the determination of key parameters (Pilavachi, 1997). Reliable simulation software allows a new CD process to be modeled using known thermodynamic and kinetic data. Values for key design parameters can be identified with a high degree of confidence. Simulation can also be applied to an existing process to study the effect of varying key parameters, and thereby provide guidelines for further optimization of the process.

2.1 Simulation Bases

Simulations in this study are based on equilibrium-stage and equilibrium-reaction model using validated experimental data. MESH (material balance, vapor-liquid equilibrium, mole fraction summations and heat balance) equations for systems in vapor-liquid and chemical equilibrium are used. The set of equation for tray j is as follows:

Material balance for component i

$$l_{i,j-1} - l_{i,j} + v_{i,j+1} - v_{i,j} + f_{i,j} + p_{i,j} = 0 \quad (2.1)$$

Vapor-Liquid equilibrium for component i

$$y_{i,j} - K_{i,j} x_{i,j} = 0 \quad (2.2)$$

Summation equation for component i

$$\sum_{i=1}^n x_{i,j} - 1 = 0 \quad (2.3)$$

$$\sum_{i=1}^n y_{i,j} - 1 = 0 \quad (2.4)$$

Energy balance for component i

$$L_{j-1} h_{j-1}^L + V_{j+1} h_{j+1}^V - L_j h_j^L - V_j h_j^V + F_j h_j^F + Q_j = 0 \quad (2.5)$$

and Chemical equilibrium

$$\prod c_{i,j}^{v_i} - K_{eq} = 0 \quad (2.6)$$

Even though no reactive distillation process will ever operate under total equilibrium conditions, an equilibrium-based model provides theoretical limits of achievable separation. Constant plate-to-plate pressure is assumed in the present model. This assumption introduces no significant error for steady-state simulations at high pressures. The present model includes IPA and DIPE as equilibrium products of the hydration and etherification reaction.

The alkene-alcohol-water-ether system is non-ideal. Consequently, the selection of physical property routines is of great importance. The UNIFAC method has been used

successfully to predict liquid phase activity coefficients and equilibrium constant expressions of similar non-ideal systems in simulation of ETBE, MEBE, TAEE, and DAA (diacetone alcohol) production processes (Podrebarac *et al.*, 1998; Sneesby *et al.*, 1997; Linnekoski *et al.*, 1997; Zhang and Datta, 1995; Delion *et al.*, 1987). UNIFAC also has been used to accurately model the vapor-liquid behavior of the IPA-water-propylene-propane system (Wyczescany, 1994). The predicted boiling points of azeotropes of IPA-water-propylene-DIPE system by UNFIC have a standard error of 0.3-5.9% comparing to experimental data. Vapor-liquid equilibrium data predicted by UNIFAC is in good agreement with the result of vapor-liquid equilibrium experiment of four-component mixture conducted in a batch reactor (Chapter 3). The UNIFAC method therefore has been shown to be suitable for the calculation of the liquid phase activity coefficients based on binary experimental vapor-liquid equilibrium data (Zavaloy *et al.*, 1993; Li and Mcketta, 1963; Cope, 1966; Barr-david and Dodge, 1959; Hancock, 1973; Ja, 1950). The Redlich-Kwong equation of state has been used to predict the non-ideal vapor phase behavior of the system. Equilibrium constants of the system were calculated using literature thermodynamics data (Mafewske and Marek, 1938; Petrus, 1986).

Commercial simulation programs most commonly used for the design of CD process include: PROIITM, AspenPlusTM, and Hysis Process. AspenPlusTM has been used successfully on the simulation of several catalytic distillation processes (Abufares and Douglas, 1995; Xu *et al.*, 1997; Eldarsi and Douglas, 1998; Nijhuis *et al.*, 1993;

Abufares and Douglas, 1995). It was found that AspenPlus™ was the program with which converged results were most readily obtained for the propylene hydration CD process. The RadFrac distillation unit built into AspenPlus™ can carry out calculation of distillation and reaction (equilibrium or kinetic model) simultaneously. It is used to obtain the data reported herein.

2.2 Catalytic Distillation Column

The core of the CD process is the catalytic distillation column (Figure 2.1). A column in which propylene hydration is to be performed has three major sections. The reaction occurs over one or more catalyst beds mounted in the middle section of the column. Rectification of the volatile components of the reaction mixture occurs in the top section. Liquid product is recovered from the bottom of a lower stripping section. We investigated CD columns with up to three catalyst beds. Hydration of propylene to IPA and IPA etherification to DIPE proceed over the catalyst simultaneously with distillation on the separation plates of the column. Unreacted volatiles rise from the reaction zone to the rectifying section where they are separated from heavier components before being removed from the top of the column. Condensed materials fall as liquid from the reaction zone into the stripping section. In the present model, an azeotropic mixture of IPA, DIPE and water is concentrated at the top of the stripping section, and enriched IPA having a very low water content is gathered at the bottom of the stripping section. The azeotrope vapor works as a carrier to lift water and DIPE back to the reaction zone for water to be further reacted with propylene and for DIPE to

equilibrate with IPA. The IPA concentration in the product stream thereby exceeds the equilibrium limit for the propylene-water-IPA reaction by continuous removal of IPA from the reaction zone.

2.3 Study of Key Design Variables

Simultaneous operation of both reaction and distillation in a single vessel leads to different responses to changes in operating conditions compared with production systems having two separate processes. It is necessary to fully understand the interaction between the processes to avoid suboptimal performance resulting from poor design. The dependence of CD column performance on each variable or combination of variables is discussed in the following section.

2.3.1 Operating Pressure and Temperature

In conventional distillation, condenser coolant and reboiler heating media temperatures determine the pressure range used. In a CD process, the selection of operating pressure must take into account the effect of pressure on the reaction zone temperature, which depends on the relative volatility of reactants, products and azeotropes (DeGarmo *et al.*, 1992).

In a CD column, the reaction zone temperature is determined by the boiling point of the liquid mixture in the catalyst bed, which in turn is determined by the composition of the liquid and the operating pressure. However, because separation and reaction occur simultaneously in the column, the composition of the liquid phase is a function of

temperature and ratio of feed rates. For the present propylene-water-IPA-DIPE system, the reaction zone temperature increases with increase in pressure. The propylene hydration reaction and IPA etherification reaction are highly exothermic. Propylene conversion decreases with an increase in reaction zone temperature. Consequently, the content of IPA in the reaction mixture is reduced with an increase in column pressure. However, the reaction rate increases with increasing temperature. Therefore, the preferred operating pressure is in a range in which the temperature of the reaction zone is sufficiently high to give a fast rate of reaction, and sufficiently low to afford a product stream rich in IPA.

Water, IPA and DIPE form two-component and three-component low boiling point azeotropes (Berge *et al.*, 1992). The compositions and boiling points of each azeotrope are presented in Table 2.1. The mole fraction of IPA in the IPA-water azeotrope varies with pressure. The IPA content climbs from 0.6670 at 0.012 MPa, passes through a maximum value of 0.6950 at 0.406 MPa, and then declines to 0.64 at 6.531 MPa (Frank and Dodge, 1959).

The relative volatility of reactants and products declines with increasing pressure. The change in the relative volatility with pressure is gradual and small, and does not significantly affect reaction and separation.

The lower limit of the operating pressure is set at conditions, which allow a reasonable reaction rate and the use of water in a condenser for recovery of unreacted propylene. The operating pressure of the CD column was varied in the range of 0.1-5

MPa. The coolant inlet temperature, reaction zone temperature, conversions of propylene and water, and product purity have been used to determine the optimum operating pressure range. For the present model, it has been found that the optimum pressure for operation of a dual catalyst bed CD column is 2 MPa.

2.3.2 Location of Reaction Zone

The location of the reaction zone in the CD column is determined by the relative volatility of reactants and products. Reactant propylene is the most volatile component and product IPA is the least volatile component of the system when IPA concentration in the liquid phase is higher than in the water-IPA azeotropic mixture. Therefore, the reaction zone is located toward the top of the column, where a high concentration of propylene is present in the liquid phase, thereby ensuring a relatively high conversion of water. The precise location of the catalyst beds depends on the optimum numbers of plates in each of the rectifying and stripping zones, which in turn depend on the feed locations and feed ratios, as will now be discussed.

2.3.3 Single and Multiple Catalyst Bed CD Columns

The CD column with a single catalyst bed optimally located at the 5th plate was modeled first, and then the potential benefits of having two or more catalyst beds were determined. A higher conversion of propylene is attainable using two spaced apart catalyst beds, the amount of the increase depending on the location and the number of catalyst beds. Higher conversion to IPA is achieved when a second bed is located at the

3rd plate, and the water feed is divided into two streams that are then fed above each of the two beds. The IPA concentration in the liquid product thereby can be increased up to 99.9 *mol%* (Table 2.2). The benefit results from improvement in the separation and reaction of propylene in the rectifying section above the catalyst bed at the 5th plate. Additional propylene is hydrated in the second catalyst bed, which would otherwise has been recycled. When a second catalyst bed is located instead at a position lower than the first catalyst bed and propylene feed, for example on the 9th plate, and no other changes are made, no benefit is observed. Instead, it was found that a detrimental interaction occurs between the phase and chemical equilibria, so the temperature of the catalyst bed on the 5th plate decreases to 324K and the IPA concentration in liquid product decreases to 99.3 *mol%* (Table 2.2). A CD column with three spaced apart catalyst beds mounted at the 3rd, 5th, and 9th plates was also modeled. Inclusion of the third bed at the 9th plate again caused the temperatures of the upper two catalyst beds to decrease. Lower temperatures in the catalyst beds led to a lower reaction rate. When the temperature is reduced, a larger amount of catalyst must be used, with a consequent decrease in efficiency and an increase in costs. The IPA concentration in the product stream of the single catalyst bed model increases to 99.9 *mol%* when the propylene/water feed ratio is increased to 3.8:1, but the conversion of propylene decreases to 26%. The CD column with dual catalyst beds mounted at the 3rd and 5th plates is the optimum configuration, having the highest level of propylene conversion and catalyst bed temperatures conferring good reaction rates.

2.3.4 Feed Location

The inlet to the column for each feed has been located so as to maximize reactant concentration in the reaction zone, without hindering the separation process occurring in the other parts of the column. In the optimum dual catalyst bed CD column configuration, liquid water is fed closely above the top of each of the catalyst beds, and propylene is fed immediately below the lower catalyst bed (Figure 2.1).

Alternative designs in which feed streams are located lower in the stripping section or higher in the rectifying section give unsatisfactory performance. Feeding reactants to the stripping or the rectifying section leads to a reduction in IPA concentration and an increase in water concentration in the liquid product. This effect is a consequence of a lower conversion of water to IPA in the reaction zone, and reduced efficiency in separation in the stripping section.

2.3.5 Stoichiometric Excess of Propylene

For an equilibrium-limited reaction, an excessive amount of one reactant is usually used to obtain a maximum conversion of another reactant to a desired product. An object of the present study is to obtain high purity IPA from the bottom outlet of the CD column. The boiling points of pure compounds and azeotropes of the propylene-water-IPA-DIPE system are listed in Table 2.1. DIPE and azeotropes that it forms are less volatile than propylene but more volatile than water and IPA, and more than 83 wt% of each DIPE azeotrope is DIPE. Therefore DIPE concentrates in the middle of the CD column (Figure 2.2). The liquid mixture in the stripping section of the CD column

comprises mainly water and IPA. The IPA-water azeotrope will only concentrate at the top of the stripping section when the IPA concentration in the total reaction mixture is higher than the concentration of IPA in the azeotrope (~ 0.67 mole fraction IPA). When a 1:1 molar ratio of propylene and water is fed to an equilibrium reactor of 410K, and chemical equilibrium is attained, the IPA molar ratio in the IPA and water mixture of the liquid outlet is only 0.15, lower than that in the water and IPA azeotrope (simulation result using equilibrium reactor model). Therefore it is necessary that the water content of the liquid mixture is consumed beyond the equilibrium limit attainable using a stoichiometric feed in order to produce high purity IPA. This is achieved by feeding an excess of propylene into the reaction zone. When the propylene/water molar feed ratio is 2.9:1, conversion of propylene to IPA in the dual catalyst bed CD column is 35%, conversion of water is substantially 100%, and the concentration of IPA in the bottom stream is as high as 99.9 *mol%*. In contrast, the equilibrium conversion of the same feed mixture is only 8.4 *mol%* at the same temperature and pressure in a conventional reactor. At feed ratios below 2.9:1 and the same operating pressure of 2MPa, IPA dehydration to propylene occurs on the upper catalyst bed due to low propylene liquid phase concentration in the bed, resulting in an increase of water concentration and decrease of IPA concentration in the liquid product stream. At feed ratios above 2.9:1, there is no significant improvement in IPA concentration in the liquid product. However, the amount and hence the cost of propylene recycle are increased.

A consequence of using a higher propylene/water ratio is a higher recycle rate of unreacted propylene. The equilibrium constant of the reaction depends on the temperature, which in turn is a function of the operating pressure. Consequently, the amount of propylene converted to product and the amount of propylene recycled vary with pressure. At 2 MPa and propylene/water molar feed ratio 2.9:1, the reaction temperature is 405K in the upper catalyst bed and 410K in the lower catalyst bed. Under these conditions, essentially all propylene consumed is converted to IPA. These values for the feed ratio and the temperature of reaction at an operating pressure of 2 MPa provide for optimum column performance while minimizing the costs for recycling propylene.

2.3.6 Distillate Flow Rate

The distillate from the CD column consists mainly of unreacted propylene and inerts carried by the propylene feed stream. Propylene is separated from the majority of propane and other impurities in a separation unit, and recycled to the CD column. Continuously feeding and recycling propylene serves to increase the propylene concentration in the reaction zone, and thereby to drive the reaction beyond the equilibrium limitation. Recycling the propylene also avoids accumulation of impurities in the reaction zone by continuously removing them from the CD column. The model has been run using both 95 wt% and 99 wt% propylene. No performance benefit accrues from the use of 99 wt% propylene. Thus the economic benefit from using 95 wt% propylene makes it the preferred feed.

In a conventional distillation column, a high distillate rate usually leads to a low liquid product flow rate, but a higher concentration of product in the liquid stream. This is not necessarily true for a CD process. Changing the distillate flow rate affects the performance of the CD column through the interaction between reaction and separation. The dependence of IPA concentration in the liquid product stream on the ratio of distillate flow rate to propylene feed rate is shown in Figure 2.3. The concentration curve of IPA is volcano shaped. The IPA concentration in the liquid product reaches the highest value (99.9 mol%) when the distillate/propylene feed molar ratio is 0.66 (Table 2.3). At the optimum temperature and pressure, DIPE forms low boiling point azeotropes with water and IPA, and remains in the upper part of stripping section and the reaction zone while high purity IPA gathers at the bottom of the column (Figure 2.2). The high concentration of DIPE in the reaction zone inhibits formation of additional DIPE, and propylene is hydrated to IPA. The liquid mixture flowing down from the reaction zone into the stripping section of the CD column consists mainly of IPA, as essentially all water is consumed in the hydration reaction. IPA and water form a low boiling point azeotrope. The IPA concentration in the liquid stream at the top of the stripping section is higher than the IPA content of the azeotropic mixture. Therefore, IPA is collected at the bottom of the stripping section and the azeotrope rises to the top of the stripping zone. Unlike conventional propylene hydration processes where extra columns are required to separate DIPE and water from IPA, no such columns are required for the CD process because azeotropes of the system work as a carrier to lift

DIPE and water up to the reaction zone and to constrain them in the middle of the CD column. Etherification does not have a detrimental effect on IPA production in the CD process when it is conducted at 2 MPa.

When the distillate/propylene ratio is lower than the optimum ratio, the conversion of propylene and water in the reaction zone must be higher, as less propylene leaves from the top of the CD column as volatile compound. A significant amount of DIPE is produced in the reaction zone due to the low concentration of water and high concentration of propylene in the catalyst beds. For example, when the distillate/propylene feed molar ratio is 0.617, the IPA mole fraction in the liquid product is only 0.88, even though total conversion of propylene is 40.4 *mol%*. Up to 8.5 *mol%* of propylene forms by-product DIPE, and only 31.9 *mol%* propylene is converted to IPA. As the distillate/propylene feed molar ratio increases, DIPE concentration in the liquid product stream decreases while IPA concentration increases (Figure 2.3). When the distillate/propylene feed molar ratio is higher than the optimum value, less propylene is consumed in the reaction zone. Therefore less IPA is formed and more unreacted water flows into the stripping section. Consequently, the water concentration in the liquid product is higher when the distillate/propylene ratio is higher than the optimum value. Thus, it is necessary to carefully control the distillate flow rate to optimize both the conversion of water and the purity of IPA produced.

2.3.7 Number of Theoretical Plates

Having determined the requirements for location of the reaction zone and the optimum feed ratio, the number of theoretical plates required for each of the rectifying and stripping sections has been determined. The dual bed CD column model has been run to determine the optimum number of plates in each section independently. The level of separation of the product usually increases with increasing theoretical plates. However, as the number of plates increases, the benefit of adding another plate becomes progressively smaller. No appreciable value accrues from increasing the number of plates in the stripping section above 21 (Figure 2.4). Similarly, no benefit accrues from increasing the number of plates in the rectifying section above two for the dual catalyst bed CD column. Thus, the dual bed CD column comprises 26 theoretical plates, of which plates 1 and 2 comprise the rectifying section; plates 6 to 26 comprise the stripping section. Catalyst beds are located on the 3rd and 5th plates with one distillation plate in-between.

2.3.8 Effect of other Operating and Design Variables

The CD column can be operated so that the reaction zone is at the temperature at which the catalyst has optimum activity. Ion-exchanged resin, tungsten oxide and zeolite have each been reported to have high activity for liquid phase hydration of propylene to IPA (Kaiser *et al.*, 1965; Petrus *et al.*, 1984). When the reaction is in the temperature range 323K to 453K, an acid ion-exchange resin catalyst (*e.g.* Amberlyst resin) can be used as the catalyst. The disadvantage for the application of ion-exchange

resins as heterogeneous catalysts is the increasing thermal instability at elevated temperature (Petrus *et al.*, 1981). Therefore, for high temperature hydration reactions it is necessary to use acidic inorganic catalysts having high thermal stability.

The feed temperature has only a slight effect on the operation of the process. However, the reaction is highly exothermic, and so feeds that are slightly cooler than the operating temperature of the catalyst beds have a beneficial effect in controlling the reaction zone temperature.

2.4 Simulation Results

Firstly, for each column configuration, the effect of varying the pressure and temperature on the process was determined. Distillate flow rate and feed ratio were adjusted to obtain optimum high purity product. Then the number of plates in the rectifying zone, above the catalyst bed(s), and in the stripping zone, below the catalyst bed(s), were varied independently, and the impact of the location of catalyst beds were examined systematically. The optimum configuration has been determined. The optimum configuration is a column having spaced apart dual catalyst beds, an upper rectifying section having two plates, and a lower stripping section having 21 plates.

2.5 Benefits of the CD Process

Simulation of the steady-state CD process (Figure 2.5) shows that the new process has advantages over conventional processes (Figure 1.1). Table 2.4 presents a detailed comparison of the state-of-the-art conventional processes and the new CD process.

Equipment for conventional propylene hydration processes usually consists of reactors with cooling system and a series of separation columns. Water is a large component of the liquid product stream. Consequently, excess water has to be removed first through distillation to obtain the azeotrope mixture. Then, extractive distillation is applied to break the azeotrope. Finally, the extractive agent remaining in the IPA has to be removed to meet the IPA product standards. Typically, four distillation columns are required to treat the product stream from a conventional reactor to get high purity IPA (Neier and Woellner, 1973). The proposed CD process consists of one column having two catalyst beds in the middle section. High purity IPA (up to 99.9 *mol%*) is obtained directly from the column.

Clearly, the CD process is much simpler to construct and operate (Table 2.4). Further, it is operated at a much lower pressure and temperature than conventional liquid phase hydration processes. Hence, the capital and operating cost are reduced dramatically, and operation is more straightforward. The CD process also offers reduction in operating costs arising from reactor cooling, catalyst recycle, and water recycle. A minor cost associated with the new process when compared with conventional direct hydration processes having high propylene conversions is the high propylene recycle ratio. An excess amount of propylene is fed to the reaction zone to ensure the maximum conversion of water, close to 100%. The optimum propylene to water feed ration ratio of 2.9:1 ensures conversion of substantially all water to IPA while minimizing costs for propylene recycle.

2.6 Kinetically Controlled CD

The optimum configuration and operation condition of the CD process for IPA production through propylene hydration were determined in the previous simulation. Simulation results showed that the CD process was practical and it had economic potential. The amount of catalyst required to achieve economic conversion has to be determined. Kinetic reaction rate equations are needed to calculate the height of reaction section and the size of the CD column. Research then proceeded to the study of kinetic of the reactions. Catalyst to be used in the CD process (Amberlyst 38) was selected. The kinetic of propylene hydration and its side reaction-IPA etherification over Amberlyst 38 were experimentally measured. Reaction rate equation was found to follow Eley-Rideal model (equations 3.27, 3.28, 3.31-3.36). The reaction rate equations of propylene hydration and IPA etherification were then incorporated into the simulation program of a CD process with a capacity of 6×10^4 tons/year. The column was designed according to the optimum configuration. In the previous simulation of equilibrium stage and equilibrium reaction model, separation on each tray was assumed to reach mass transfer equilibrium and reactions in reaction zone were assumed to reach chemical reaction equilibrium. In the kinetic controlled model, kinetic reaction rate equation were used to calculate reaction rate in the catalyst reaction zone. Reactions were assumed to reach 90% of equilibrium conversion on the reaction trays and a typical tray efficiency of 0.7 was applied to all separation trays. The process (Finger 2.5) was then simulated to determine the size of the CD column.

Simulation result showed that a CD column of 26 separation stages and two reaction zones was needed to produce 99.9 *mol%* IPA. Stage 3rd and 5th are the reaction stages with catalyst loaded on them. Propylene stream of 95 *vol%* purity is fed above the 6th stage at a flow rate of 348 kmol/hr. Inert of the propylene feed stream is represented by propane. Two streams of water are fed into column separately on the 3rd and 5th stage at 30kmol/hr and 90kmol/hr. Under 2 MPa, the temperature of condenser and reboiler are 353K and 489K respectively, while the temperature of the upper reaction stage and the lower reaction stage are 408K and 418K. IPA liquid product stream gathered from the bottom of the CD column is of 99.9 *mol%* purity. The liquid product flow rate is 118 kmol/hr. The column diameter is 5.5 meter. The catalyst bed height of the upper reaction stage is found to be 0.8m; the height of the lower reaction stage is 2.1m. With 0.61m spacing for each separation stage, the height of the CD column would be 18.7m (Figure 2.6). Simulation program and stream table of the process was attached in appendix.

2.7 Conclusions

Catalyst distillation technique was applied to IPA production through propylene direct hydration. Steady state simulation of the process was carried out and a process flow sheet was developed. The optimum operating parameters for the catalytic distillation column for the production of IPA were determined using a computer model. The simulation result indicated that the use of CD process overcomes chemical and vapor-liquid equilibrium limitations. The model showed that high purity IPA (up to 99.9

mol%) can be produced as a liquid product stream containing virtually no water, in contrast to conventional processes. The reduction of water content below the azeotrope water content occurs by reaction of water with a 2.9:1 optimum molar excess of propylene when using a CD column having two spaced apart catalyst beds. Excess propylene is recycled to remove impurities that may otherwise accumulate in the CD column. The equilibrium ether content of the reaction mixture is retained in the reaction zone, which reduces the effect of side reaction. The optimum operating pressure is 2MPa for the CD column having two spaced-apart catalyst beds. Simulation of the CD column of the above configuration and operation condition with reaction rate controlled by kinetic equations was also carried out to size the column. The separation tray efficiency was assumed to be 0.7. The result showed the column was 18.7m high, with 0.8m high upper catalyst bed and 2.1m high lower catalyst bed.

2.8 Nomenclature

c	component concentration in liquid phase, mol/L
f	component feed flow rate, mol/hr
F	total feed flow rate, mol/hr
h	component molar enthalpy, J/mol
K_{eq}	reaction equilibrium constant
l	component tray liquid flow rate, mol/hr
L	total tray liquid flow rate, mol/hr
P	component tray formation rate, mol/hr
y	component molar vapor fraction
x	component molar liquid fraction
v	component tray vapor flow rate, mol/hr
V	total tray vapor flow rate, kmol/hr
Q	tray heat withdraw, J/hr

Subscripts

i	compoment
j	distillation tray

Superscripts

F	feed
L	liquid phase

V vapor phase

v stoichiometric coefficient

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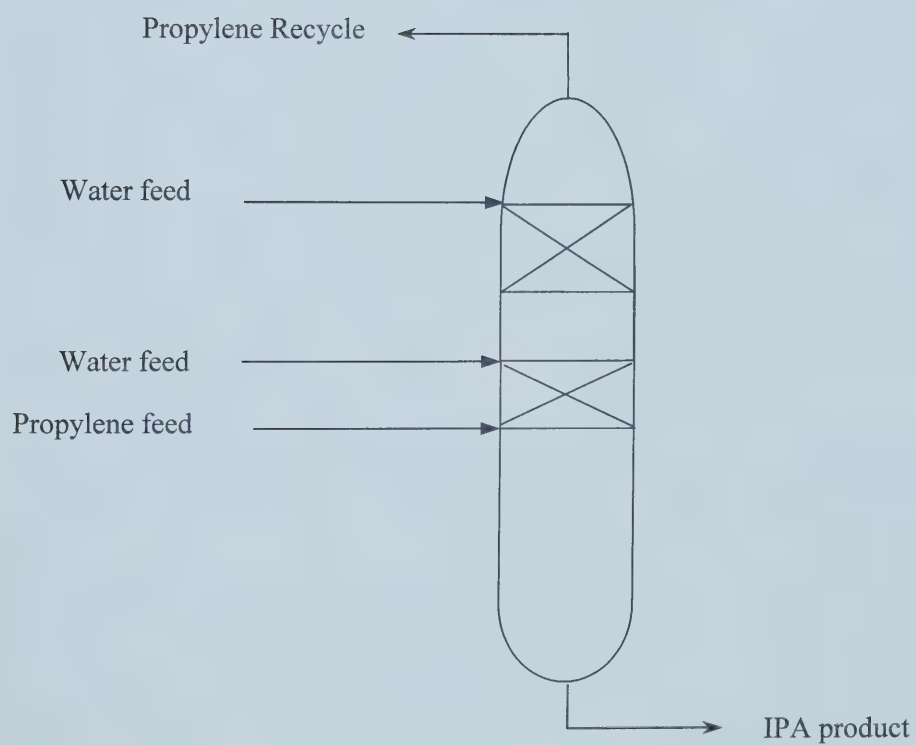


Figure 2.1 Configuration of dual catalyst bed catalytic distillation column

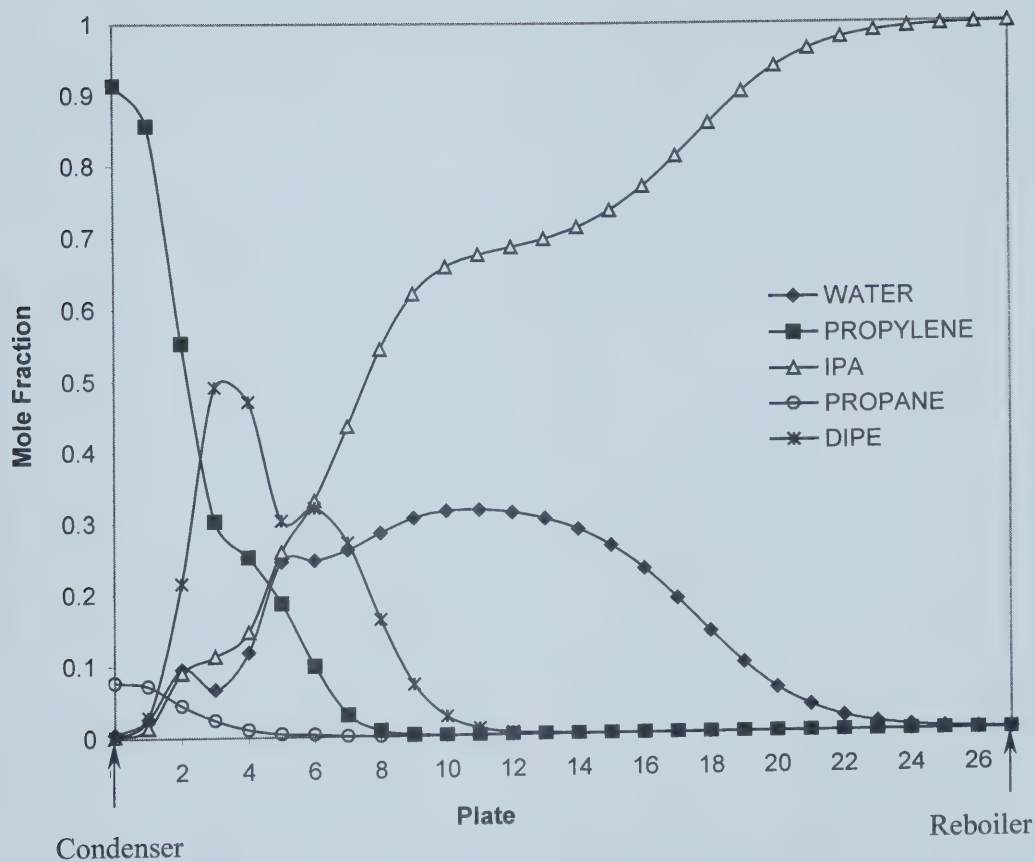


Figure 2.2 Liquid phase composition profile of dual catalyst bed CD column

(propylene/water molar feed ratio=2.9:1)

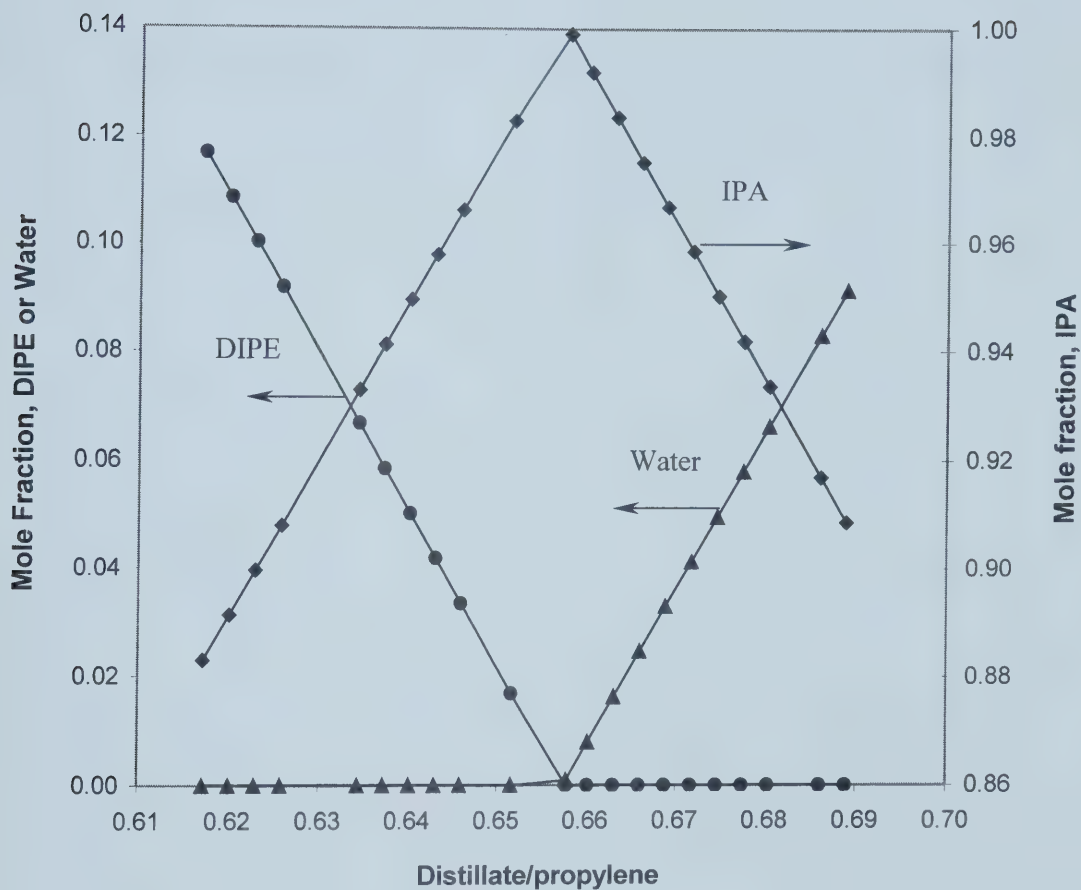


Figure 2.3 Effect of distillate flow rate on dual catalyst bed CD column performance (propylene/water molar feed ratio=2.9:1)

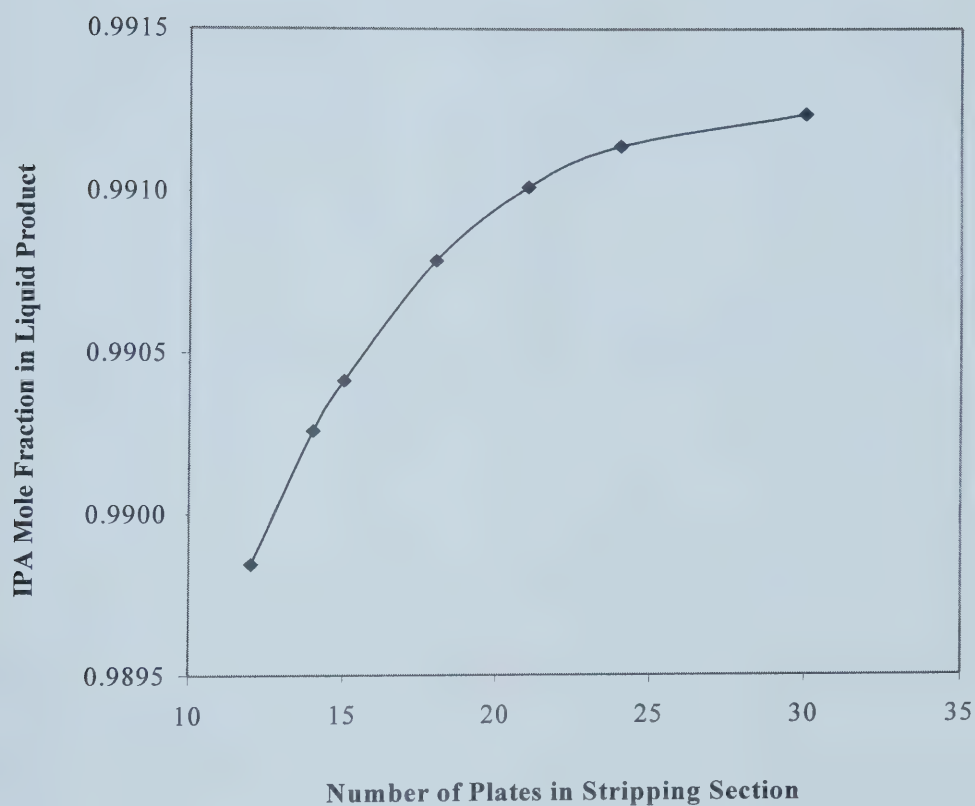


Figure 2.4 Effect of the number of stripping plates on CD column performance (water/propylene molar feed ratio=1:2.9; distillate/propylene molar ratio=0.67)

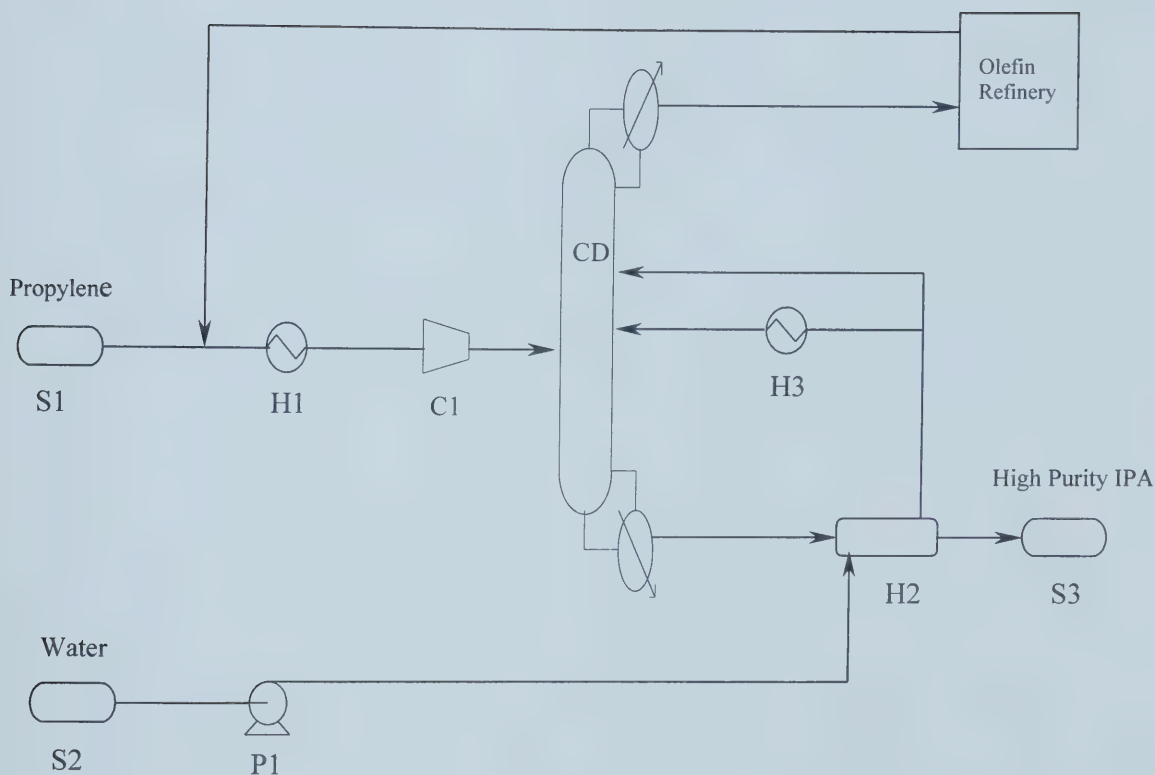


Figure 2.5 Flow diagram of catalytic distillation isopropyl alcohol process

CD catalytic distillation column

H1, H2, H3 heat exchangers

S1, S2, S3 storage tanks

P1 pump

C1 compressor

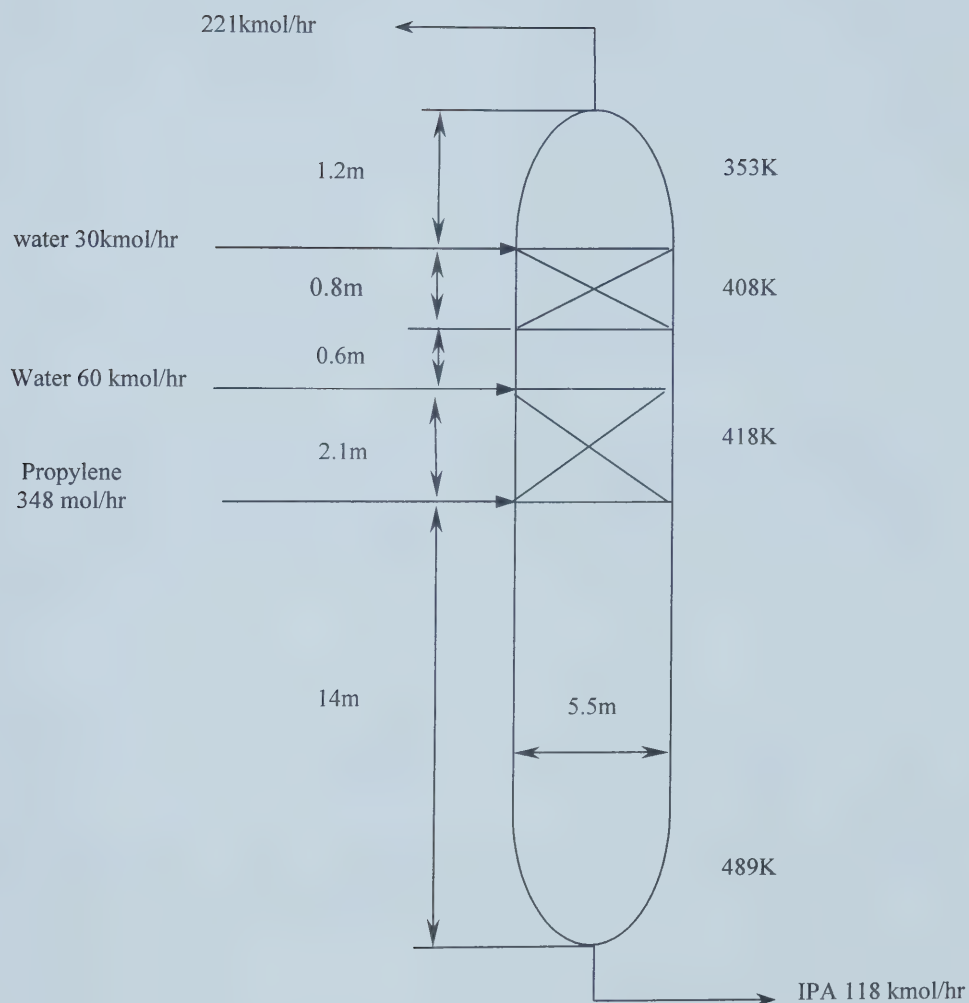


Figure 2.6 Size of a CD column

Table 2.1 Azeotropes of Water-IPA-DIPE System

compound or azeotrope	boiling temperature of component and azeotrope (K)	composition of azeotrope		
		water wt%	IPA wt%	DIPE wt%
propylene	225.43			
water	373.13			
IPA	355.65			
DIPE	342.15			
water+IPA	353.45	12.6	83.7	0
IPA+DIPE	339.35	0	16.3	83.7
water+DIPE	335.35	4.5	0	95.5
water+IPA+DIPE	334.75	4.7	7.3	88.0

IPA: isopropanol DIPE: diisopropyl ether

Table 2.2 Comparison of Multiple and Single Catalyst Bed CD Column

catalyst bed	catalyst bed temperature (K)			IPA mole fraction in liquid product	propylene/water feed molar ratio	propylene conversion* mol%
	3rd plate	5th plate	9 th plate			
1		409		0.994	2.9:1	34
1		410		0.999	3.8:1	26
2		324	409	0.993	2.9:1	34
3	322	324	409	0.993	2.9:1	34
2	405	410		0.999	2.9:1	35

* 35% conversion of propylene is equivalent to 100% conversion of water when the propylene/water feed molar ratio is 2.9:1

Table 2.3 Effect of Distillate/Propylene Ratio on CD Column Performance

distillate/propylene feed molar ratio	0.617	0.658	0.689
IPA mole fraction in product stream	0.883	0.999	0.909
total propylene conversion mol%	40.40	36.18	32.86
water conversion mol%	99.80	99.80	90.60
propylene conversion to IPA mol%	31.94	36.15	32.85
propylene converison to DIPE mol%	8.466	0.027	0.012

*water/propylene molar feed ratio=1:2.9

Table 2.4 Comparison of Propylene Hydration Processes

direct hydration process	fixed-bed vapor phase	liquid phase	catalytic distillation
PRO feed stream (wt%)*	99	95	95
catalyst	WO ₃ -ZnO/H ₃ PO ₄	aqueous silicotungstat	**
catalyst regeneration	no	yes	no
reactor	yes	yes	no
cooling of reactor	yes	yes	no
distillation column in process	4	4	1
operating pressure (MPa)	2.5-6.6	20.3	2
operating temperature (K)	513-523	513-563	323-460
feed ratio (water/PRO)	1:4-10	N.A.	1:2.9
PRO recycle/feed mole ratio	94-95%	30-40%	65%
water recycle/feed mole ratio	40-80%	N.A.	0
conversion	5-6% PRO	60-70% PRO	35% PRO, >99% water
IPA selectivity	96%	98-99%	>99.9%

* PRO=propylene

** for example, zeolite or proton-exchanged resin

CHAPTER 3

KINETIC STUDY OF LIQUID PHASE PROPYLENE DIRECT HYDRATION

3.1 Introduction

3.1.1 Propylene Hydration Catalyst

Catalyst that is effective for the direct hydration of propylene is acidic in nature. Some of the direct hydration processes previously described in the literature use supported mineral or inorganic acid in a relatively low pressure, essentially vapor phase process for propylene hydration. Suitable catalysts include silicophosphoric acid, phosphoric acid on Celite, and tungstic acid on alumina. The catalyst that can be used in propylene direct hydration process must have hydrothermal stability in the presence of liquid phase water at the required reaction temperature. The most commonly utilized catalyst for this process is tungsten oxide (Kaister, *et al.*, 1962). Acid zeolites and supported Group VI and Group VIII metals have also been reported to be active in the hydration of propylene (Eguchi, 1987; Iwamoto, 1986; Fajula, 1984).

Ion-exchange resins were found to be effective for the direct hydration of olefins at selected process conditions (Kaister et al, 1962; Petrus et al, 1984; Delion, 1987). Equilibrium conversion to IPA can be obtained with ion-exchange resin at process temperature lower than previously found necessary with other catalysts. Since the high activity displayed by ion-exchange resins occurs at lower process temperature, process

can be operated at conditions where hydration reaction and product separation through distillation can proceed simultaneously. The activity of ion-exchange resins, which appear to be superior solid catalyst for propylene hydration CD process, must be confirmed by experiment.

Ion-exchange resins are cross-linked three-dimensional structures of polymeric substances obtained by sulphonation of copolymer made of polystyrene and divinyl benzene. They offer many advantages over other acid catalysts. The easy elimination of the reaction medium and the possible reutilization of ion exchange catalysts make them preferable to inorganic acids and bases. However, these resins are not suitable for use at temperature above 180°C.

There are gel type and macroporous type resins. When the gel type resin is used in an aqueous solution, it is in highly expanded state and has highly developed pore structures, but when it is in contracted state, the pore structures are lost. While the “macro-reticular” pore structure built into the macroporous type resin is not lost when the resin is in its contracted state.

3.1.2 Reaction Mechanism

Catalysis systems can be classified as homogeneous or heterogeneous. In homogeneous catalysis, a small catalyst molecule or ion is consumed in an early reaction step and is restored in a later step. In heterogeneous catalysis, the forces active at a solid surface distort or even dissociate an adsorbed reactant molecule to increase the rate of reaction. In the case of catalysis by ion exchange resins this classification is not

as clearly defined (Helfferich, 1988). In macroporous resins, the reaction medium is distributed between gel and pores phases (Frankel, 1971). Chakrabarti and Sharma (1993) pointed out that most resin-catalyzed reaction could be classified either as quasi-homogeneous or quasi-heterogeneous.

Two approaches are followed for ion exchange resin catalyzed reactions. The first one envisions the resin to behave like a dissolved electrolyte. Reactions are treated as homogeneous reactions in the liquid phase. In the other approach, the resin is treated like a solid porous catalyst, in a manner similar to heterogeneous catalytic reactions.

Kaiser (1962) studied the hydration of propylene in a trickle bed reactor using Amberlyst 15, a macroporous resin, and Amberlite IR-120, a gel type resin. When water-rich phase was the continuous one, both resins showed similar catalytic activity. A pseudo-first order model was obtained to represent the data in the kinetic study.

Petrus (1984, 1986) studied the kinetics of the hydration of linear butenes and propylene over a strong acid ion-exchange resin and proposed a scheme with carbenium ion as intermediate. But Velo (1988) found in his study of the liquid-phase hydration of isobutene to tert-butyl alcohol that the reaction mechanism put forward by Petrus (1984) to account for the hydration of olefin seemed to fail in predicting the intrinsic rates in the case of isobutene hydration in the presence of large concentrations of product.

The etherification reaction accompanied the propylene hydration was usually treated as an insignificant side reaction. Investigations on propylene hydration or IPA dehydration were carried out with excessive amount of water, and no appreciable

amount of DIPE formed under those test conditions (Mourgues, 1967; Kuo, 1999; Kaister, 1962; Majewski, 1938). Kinetics on the etherification of olefins with 4 to 6 carbons with methanol or ethanol to produce ethers (MTBE, ETBE, TAME, TAEE) as important additives in gasoline were well studied (Rehfinger, 1990; Zhang, 1995; Rihko, 1997; Subramaniam, 1987; Ancillotti, 1977; Linnekoski, 1997). Improved interpretation is often obtained using approaches traditional to heterogeneous catalysis and based on classical models such as Eley-Rideal type (E-R) and Langmuir-Hinshelwood type (L-H).

In the study of liquid phase synthesis of MTBE from methanol and isobutene using the ion exchange resin catalyst, Amberlyst 15, Suvramaniam (1987) concluded that both homogeneous and heterogeneous kinetic models based on L-H type correlated the data of MTBE formation satisfactorily.

Rihko (1997) found in his study of etherification of isoamylene with methanol that experimental results were best described by kinetic equations based on L-H model with alcohol and ether adsorbed on the catalyst surface and isoamylene reacted from the bulk liquid phase, while homogeneous reaction mechanism had the largest standard deviations of parameters.

Linnekoski (1997) used three kinetic models: homogeneous, Eley-Rideal type, and Langmuir-Hinshelwood type to fit the measured reaction rates of liquid-phase formation of TAEE through reaction between ethanol and isoamylene catalyzed by the acid ion-exchange resin (Amberlyst 16W). The statistics showed that L-H type model gave a

better fit with experiment data. But the fit was not so good at low ethanol mole fractions (<0.4), which could indicate that the mechanism changes with decreasing alcohol mole fraction.

3.1.3 Effect of Polar Component on Reaction Mechanism

The reaction mechanism occurring in the presence of resin depends on the polarity of the reaction medium, as shown by vapor phase kinetic studies carried out on dehydration reactions of alcohols such as methanol, ternary butyl alcohol and IPA by Thronton (1974) and Gates (1973).

Sonnemanes (1993) investigated the vapor phase hydration and etherification of propylene over acidic zeolites and concluded that the kinetics of propylene hydration over H-ZSM-5 was of a L-H type. The hydration and etherification reactions were significantly influenced by reactant adsorption. The catalytic activity of aluminum-rich H-ZSM-5 for both reactions decreased with increasing Brønsted acid site concentration (aluminum content) because the polar reactants became too strongly adsorbed.

Linnekoski (1997) reported the formation of TAEE in the liquid-phase through reaction between ethanol and isoamylenes catalyzed by the acid ion-exchange resin, Amberlyst 16W. When azeotropic mixture of ethanol and water was used as reactant, a decrease in the overall olefin conversion was observed. The change in conversion can be due to the competitive adsorption of water, ethanol and olefin. When water is added to the system it competes for the active sites with ethanol and olefin and fewer olefins are protonated by the active sites, which in turn results in lower conversion. Comparing

with ethanol, water gives a more basic solvated proton of lower activity which gives lower overall conversion as indicated in the literature. It's also observed that hydration yield (reaction between isoamylene and water) was about the same as the etherification yield (reaction between isoamylene and ethanol) although the ethanol/water molar ratio was as high as 11, indicating a competition between water and ethanol with protonated olefin. Water, as the stronger nucleophile, is preferred in the competition. The stronger nucleophilicity of water can be realized by comparing the dielectric coefficients of water and ethanol (Linnekoski et al, 1998).

The study on the liquid phase hydration of propylene over a gel type resin catalyst, Dowex 50WX8, was carried out by Heistand (1961). It was found that the addition of IPA to the feed resulted in a decrease of reaction rate. Typically the reaction rate decreased by about a factor of 2 when the mole fraction of IPA in the water-rich feed was increased from 0 to 0.1.

Petrus (1986) studied liquid phase hydration of propylene catalyzed by Imac C8P at low IPA concentration (0.5%, 5%, 10 wt%). It was also found that the presence of IPA led to a larger reduction in reaction rate than expected.

The kinetics of propylene hydration and IPA etherification is needed for the accurate modeling of the IPA production CD process. No study on the kinetics of liquid phase propylene hydration and IPA etherification over ion-exchange resin at high IPA concentration is available in literature.

3.2 Experimental

3.2.1 Experimental Apparatus

All experimental runs were performed in a batch slurry reactor system (Figure 3.1). The reactor is a high pressure Parr reactor (Model 4841, Parr Instruments Inc. USA) made of SS-316 stainless steel. The reactor has a volume of 320 mL and is equipped with an impeller. A thermocouple (J-type) was used to measure reactor temperature. The heating device/controller was used to maintain a constant reactor temperature within $\pm 0.5\text{K}$. Reactor pressure was measured using a pressure transducer (Foxboro electronic transmitter, Model 841 GM-D) at an accuracy of ± 1 psi. The liquid sampling line consists a 1/16 inch o.d. stainless steel tube in the reactor and a 1/8 inch o.d. stainless steel tube outside of reactor connected to a stainless steel needle valve. The vapor sampling line was a 1/8 inch o.d. stainless steel tube connected to a needle valve. A septum was mounted by a nut and mental net on the outer tube at the end close to the reactor on each sampling line. The vapor sampling line was heated with heating rope to 393K. The end of the vapor sampling line was connected to a bubble flow meter, which was used to measure the amount of purged vapor.

3.2.2 Chemicals and Catalysts

Isopropyl alcohol and diisopropyl ether were obtained from Aldrich in analytical reagent grade. They were used as received.

Amberlyst 38, sulfated zirconia, zeolites 13X (Aldrich, 20,3864-7), SAPO-5 (MHZN2-34, Laval University, PQ, Canada) and silicalite with an alumina binder (S-115 Al_2O_3) were chosen for preliminary test. The preliminary test showed that Amberlyst 38 had a better activity and was chosen for detailed studies (Figure 3.2). The typical physical and chemical properties of Amberlyst 38 are listed in Table 3.1.

3.2.3 Analysis Techniques

Both vapor and liquid samples were analyzed using a Hewlett Packard 5890 Series II Gas Chromatograph equipped with a thermal conductivity detector (TCD). A 30m×0.32mm ID fused silica capillary column was used to separate water, propylene, IPA and DIPE in liquid samples. Vapor phase components were separated using a 1/8 inch o. d., 8 feet long column packed with 50-80 mesh Porapark R. Helium was used as carrier gas.

For the liquid sample analysis, the operating conditions for the gas chromatograph were:

Temperature (°C)	Injector: 150
	Detector: 150
	Oven: 45, 2 min→ 50/min→ 180, 2 min

The sample injection size was 2 μL . The approximate retention time for the four components under the above operating conditions were:

Water:	1.4 min
--------	---------

Propylene: 1.9 min

IPA: 4.4 min

DIPE: 5.2 min

For the vapor sample analysis, the operating conditions for the gas chromatograph were:

Temperature (°C) Injector: 150

Detector: 150

Oven: 110, 1 min → 20/min → 200, 2 min

The approximate retention time for the four components under the above operating conditions were:

Propylene: 3.8 min

Water: 4.2 min

IPA: 7.9 min

DIPE: 14.3 min

3.2.4 Experimental Procedure

In a typical kinetic reaction run, about 220 mL mixture of known amount IPA, deionized water, and DIPE was placed in the reactor. The ion-exchange resin catalyst, Amberlyst 38, was put into the reactor after washing with water, drying at 115°C for 5hrs and weighting. The reactor was then purged with helium to provide an inert atmosphere. The reactor was closed and heated to the desired reaction temperature, between 384-421K. The stirrer was started at the moment the reactor content reached

the set temperature and reaction time was set as zero. No corrosion of the reactor was observed.

About 2 μ L of liquid sample and 35 μ L vapor phase sample were withdrawn from the reactor every 20-25 minutes for analysis. The time and the pressure of the sampling were recorded. Before sampling, the liquid sampling line was purged with about 1.0 mL liquid content of the reactor to make sure that sampling was not affected by dead volume in the sampling line. The vapor sampling line was purged with 1.5mL vapor content of the reactor. The pressure of the reactor was not significantly affected by the sampling process. Liquid sample was taken from the sampling line using a syringe and injected immediately into the GC. Vapor sample was taken from the vapor sampling line with a SUPLCO sample lock syringe and injected into the GC immediately. Syringe adaptors were used to ensure that same amount of sample was taken for analysis each time. The amount of liquid and vapor removed from the reactor was negligible. The pressure of the system increased as the propylene and DIPE were produced while reactions proceeded. The pressure can rise to 350 psig or more depending on reaction temperature, initial mixture composition and catalyst loading. The molar ratios of initial feed components were DIPE: IPA : water =2-1.2:1.8-0.7:1.

For the tests of vapor-liquid equilibrium of propylene-water-IPA-DIPE four-component system, a mixture of IPA-water-DIPE was charged into the reactor. The gas inlet and outlet valve were opened to purge the reactor with propylene for 5 seconds. Then the gas outlet valve was close to filled the reactor with propylene. Stirrer was

started to facilitate the solving of propylene into the liquid mixture. The initial pressure of the reactor was 110-180 psig. The system was heated to the desired temperature (393-423K) and maintained at steady state for 1.5 hours to ensure that phase equilibrium has been reached before vapor and liquid phase sample were taken for analyses.

3.3 Results and Discussion

3.3.1 Catalyst Screening

The dehydration of IPA is widely used as a reaction to qualitatively characterize the activity of solid catalyst and to study the mechanism of the catalytic dehydration of alcohols over solid acids. Those studies provided useful information concerning the activity of catalyst for propylene hydration and etherification reactions. Rivard (2000) studied the performance of the well known acid catalysts including alumina, zeolites 13X, SAPO-5 and silicalites in IPA dehydration reaction with an initial IPA concentration of 10 wt% at 463K. Silicalite with an alumina binder (S-115 Al₂O₃ ExT.) was found to be the most active catalyst among the catalysts tested. Kaiser *et al.* (1962) concluded from experimental results of propylene hydration over ion-exchange resin that conversion and selectivity similar to those obtained with inorganic catalysts could be obtained with ion-exchange resins at milder conditions of lower temperatures and pressures. Two strong acidic ion-exchange resins of the sulfonic acid type (Rohm and Hass Co., Amberlyst 15 and IR-120) were used. The Amberlyst 15 differs from the IR-120 in that it has a “macro-reticular” pore structure built into the resin which is not lost

when the resin is in its contracted state. Neither resin was found to be significantly different from the other in any of the areas examined in the study. This was attributed to the fact that the resins were in an aqueous solution, where both resins were in highly expanded states and had highly developed pore structures.

Catalysts chosen for the preliminary tests were Amberlyst 38, a strong acidic ion-exchange resin reported to be thermally stable up to 433K, Silicalite with an alumina binder (S-115 Al₂O₃ ExT.), zeolites 13X (Aldrich, 20,3864-7), SAPO-5 (MHZN2-34, Laval University, PQ, Canada) and sulfated zirconia. Test runs were carried out at 411K. Amberlyst 38 was found to be the most active catalyst among the screened samples (Figure 3.2).

3.3.2 Mass Transfer Limitations

Heterogeneous catalytic reactions can be said to occur through the following steps

1. transport of reactant material(s) from bulk liquid through boundary layer to the catalyst surface
2. diffusion of the reactant(s) through the pores to the active catalyst surface
3. adsorption of the reactant(s) onto the active site(s)
4. catalytic surface reaction to form reaction product(s)
5. desorption of product(s) from the active site(s)
6. diffusion of reaction product(s) through the pores to the catalyst surface
7. transport of the product(s) through boundary layer to the bulk media

The external mass transfer is described in steps 1 and 7. Internal mass transfer through the porous catalyst via molecular and Knudsen diffusion is described in steps 2 and 6. The reaction, which consists of the adsorption/desorption of the reactants/products and the surface reaction are detailed in steps 3-5. The observed rate of reaction depends on all of the above steps. True surface reaction rates can only be determined if the experiments are performed under conditions where the observed rate is not limited by diffusional processes.

3.3.2.1 Effect of Stirring Speed

The region where the external mass-transfer is no longer rate limiting was determined by varying the stirrer speed. The rotating speed of the stirrer in the reactor was changed while initial charge of reactants and catalyst remain the same (220mL IPA, DIPE and Water mixture, DIPE:IPA: water=1.5:1.8:1, catalyst loading 3.8 wt %, 421K). During the pre-trial runs, it was found that the stirrer speed had no effect on the reaction rate above stirring speed 800rpm at the above reaction conditions (Figure 3.3).

When the stirred speed was reduced to 150rpm, the pressure of the reactor increased faster than that of stirring speed of 800rpm or 1200rpm. The possible reason was that the vapor and the liquid phase in the batch reactor were not in vapor-liquid equilibrium as we assumed when low stirring speed was employed. Propylene and DIPE formed in liquid phase escaped into vapor phase without saturating the liquid due to the lack of agitation. A test was repeated to verify our suspect. A 150 mL mixture of DIPE, IPA and water at a molar ratio of 1.5:1.8:1 was charged into the reactor. The

vapor phase was first purged with helium, and then filled with helium, which is of negligible solubility in the mixture. The pressure changes of the closed system with time with no stirring and a stirring speed of 1200rpm were recorded. Similar tests were performed again but with vapor phase filled with propylene. It can be seen from Figure 3.4 that the pressure of the system remained the same as time elapsed when vapor phase was filled with helium. Stirring of liquid made no difference to the system pressure. When the vapor phase was filled with propylene and no stirring of liquid was provided, the pressure of the system decreased gradually as time passed by. In the case of stirring, the pressure of the system with a propylene vapor phase decreased drastically and reached steady point within 0.5 minute. The results of this test (Figure 3.4) proved that stirring facilitated the dissolution of propylene into the liquid, therefore accelerated the vapor-liquid equilibrium process. Stirring affects not only external mass transfer but also the vapor-liquid equilibrium of the system. Sufficient stirring speed should be used to ensure that reactants and products in vapor and liquid phase are in equilibrium and reactions are carried out in the zone of no external mass transfer effect. In all experimental runs, a stirrer speed of 1200rpm was employed to eliminate the effect of stirring speed on the overall reaction rate and the equilibrium state of vapor and liquid phases. In reaction runs, propylene was produced gradually and samples were taken to determine the compositions of both liquid and vapor, the retention time of propylene solving into liquid (0.5min) do not affect experimental results.

3.3.2.2 Effect of Catalyst Particle Size

The region where the internal mass-transfer is not rate limiting was determined by varying the catalyst particle size. Tests at 421K with catalyst loading of 3.8 wt% and DIPE: IPA: water ratio of 1.5:1.8:1 indicated that internal mass transfer was not rate limiting at particle size ranges of 20-40 and 40-100 mesh under the test conditions (Figure 3.5). The macro structure in Amberlyst 38 permits ready access of liquid reactants to active sites present throughout the resin beads. There is no major resistance for the reactants to diffuse into the pores and the products to diffuse out under the test conditions.

3.3.3 Reusability of Catalyst

Amberlyst 38 resin can be used at temperature up to 433K. General desulfurization resulting in loss of activity may be evident at higher temperature. To avoid fouling, poisoning or degradation, it is necessary to prevent the catalyst from the contact with colloidal particles, inorganic salts and organic peroxides to prevent deactivation of the catalyst.

In this study, precautions were taken to prevent the decrease on the catalyst effectiveness. The reusability test was conducted by using the same catalyst in two runs with similar operation conditions (220mL DIPE, IPA and Water mixture, DIPE: IPA: water=1.5:1.8:1, catalyst loading 3.8 wt%, 421K). Figure 3.6 shows the results from these two runs. No indication of deactivation was observed for the reused catalyst.

3.3.4 Catalyst Loading

The effect of catalyst loading on the rates of propylene and DIPE formation was determined by performing kinetic runs at catalyst loadings of 1.8 wt%, 2.7 wt% and 3.8 wt%. The experiments were performed at 421K with DIPE: IPA: water initial ratio of 1.5:1.8:1. As can be seen in Figure 3.7, the calculated kinetic parameters were not affected by catalyst loading.

3.4 Kinetic Modeling

3.4.1 Calculation of Reaction Rate

The system we studied involves two reactions in series while each of them is reversible. The rate of the reversible hydration and etherification are expressed in terms of propylene and DIPE. The rate of propylene and DIPE formation per gram of catalyst per minute in a batch slurry reactor can be written in the following manner:

$$r_i = \frac{1}{m_c} \frac{dN_i}{dt} \quad (3.1)$$

The content of batch slurry reactor consists of a liquid phase where hydration and etherification proceed over the suspended solid catalyst and a vapor phase where the reactants, products and inert are present. It is assumed that the amount of inert, helium, dissolved in liquid phase was negligible. The total amount of propylene and DIPE formed at the time corresponding to each sampling was calculated using the equations of material balance.

Mass balance:

$$M_a(L^*x_a+V^*y_a)+ M_w(L^*x_w+V^*y_w)+ M_p(L^*x_p+V^*y_p)+ \\ M_e(L^*x_e+V^*y_e) = M_{total} \quad (3.2)$$

Chemical Reaction:

$$L(x_p+2x_e)+ V(y_p+2y_e) = N_{a0}+ 2N_{e0}-(L^*x_a+V^*y_a) \quad (3.3)$$

3.4.2 Determination of Rate Equation

Homogeneous Approach

By combining terms and using the equilibrium constants for the reactions, we obtain the rate equations for the formation of IPA and DIPE in the expression of homogeneous systems:

$$r_p=k_{11}(C_wC_p-C_a/K_{E1}) \quad (3.4)$$

$$r_e=k_{22} (C_a^2-C_eC_w/K_{E2}) \quad (3.5)$$

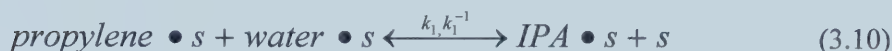
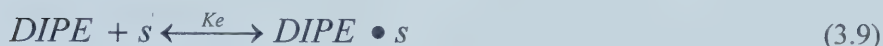
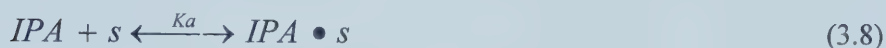
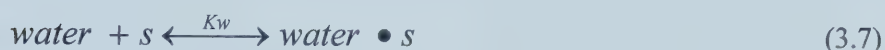
Heterogeneous Approach

The rate laws developed for surface catalysis are based on the following assumptions:

1. The surface of the catalyst contains a fixed number of site;
2. All the active sites are identical;
3. The activities of these sites depend only on temperature. They do not depend on the nature or amounts of reactants and products present on the surface during the reaction.

Langmuri-Hinshelwood (L-H) kinetics is derived by assuming that the surface coverage in catalytic rate laws is given by the equilibrium coverage, which exists in the absence of the surface reaction. The resulting rate expressions find wide use in the chemical industry because they exhibit many of the commonly observed features of surface-catalyzed reactions.

Propylene hydration and IPA etherification can be represented by the following mechanism:



The L-H model assumes that the reaction takes place between reactants adsorbed on two acid sites. Of all these elementary reaction steps (Equations 3.6-3.11), one step is considered to be rate-determining, all other steps are considered to be at equilibrium. When surface reactions (3.10) and (3.11) are the rate-determining steps, the overall rate of hydration and etherification can be expressed in terms of propylene and DIPE formation rate using the fraction of sites occupied by adsorbed components as:

$$r_p = k_1^{-1} \theta_a \theta_v - k_1 \theta_p \theta_w \quad (3.12)$$

$$r_e = k_2 \theta_a^2 - k_2^{-1} \theta_e \theta_w \quad (3.13)$$

The rate of adsorption of component i is given by the Langmuir model as:

$$r_{ads(i)} = K_{ads(i)} \theta_v C_i - K_{dea(i)} \theta_i \quad (3.14)$$

where the fraction of active sites which are vacant, θ_v , can be expressed as:

$$\theta_v = 1 - \theta_a - \theta_w - \theta_p - \theta_e \quad (3.15)$$

The rates of adsorption of all the components are considered to be at equilibrium.

Setting Equation 3.14 to zero yields:

$$\theta_i = K_i \theta_v C_i \quad (3.16)$$

The equilibrium adsorption constant for component i, K_i , is defined as:

$$K_i = \frac{K_{ads(i)}}{K_{dea(i)}} \quad (3.17)$$

The fraction of active sites occupied by component i can be written as:

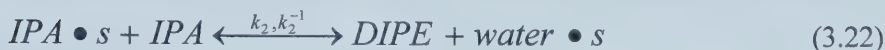
$$\theta_i = K_i C_i \theta_v = \frac{K_i C_i}{1 + \sum K_i C_i} \quad (3.18)$$

then the formation rates of propylene and DIPE are:

$$r_p = \frac{k_1^{-1} K_a C_a - k_1 K_p K_w C_w C_p}{(1 + K_a C_a + K_w C_w + K_p C_p + K_e C_e)^2} \quad (3.19)$$

$$r_e = \frac{k_2 K_a^2 C_a^2 - k_2^{-1} K_w K_e C_w C_e}{(1 + K_a C_a + K_w C_w + K_p C_p + K_e C_e)^2} \quad (3.20)$$

Eley-Rideal (E-R) type of rate models assumes that the reaction takes place between one molecule adsorbed on one acid site and one nonadsorbed molecule from the liquid phase:



$$r_p = \frac{k_1^{-1} K_a C_a - k_1 K_w C_p C_w}{1 + K_a C_a + K_w C_w + K_p C_p + K_e C_e} \quad (3.23)$$

$$r_e = \frac{k_2 K_a^2 C_a^2 - k_2^{-1} K_w C_w C_e}{1 + K_a C_a + K_w C_w + K_p C_p + K_e C_e} \quad (3.24)$$

In these models the summation in the denominator accounts for all the adsorbed species that share the largest portion of acid sites. L-H type and E-R type models with adsorption as rate-determining step can be obtained using the same procedure. Taking adsorption as rate-determining step, reaction rate can be written as Equation 3.14.

According to Helfferich (1962), the adsorption of the strongly polar components on ion exchange resin are much stronger than the adsorption of the less polar components. Rehfinger (1988) performed study on adsorption behavior of n-butane, 1-butene and methanol on ion exchange resins. Sorption and swelling experiments confirmed the highly selective methanol absorption into the gel microspheres. Over the whole concentration range of interest, only the alcohol was in the gel phase and other

components were displaced. In pure liquids the amount of methanol moles adsorbed is about 3.5 times that of 1-butene. The ratio was independent of the degree of cross-linking of the resin. Liquid phase adsorption experiments conducted for methanol, ethanol, C₅ and C₆ olefins and dibutyl-ethers on ion-exchange resin by Zhang (1995) provided direct experimental evidence validating the most abundant surface species assumption for ethanol and the neglect of the olefin and ether adsorption in rate expressions.

To simplify the equations, term $K_p C_p + K_e C_e$ is omitted as it was later calculated to be 0.7-1.2% of the term $1 + K_a C_a + K_w C_w$ from experimental data. The rate equations can be simplified to:

L-H type:

$$r_p = \frac{k_1^{-1} K_a C_a - k_1 K_w K_p C_w C_p}{(1 + K_a C_a + K_w C_w)^2} = \frac{K_{p1} C_a - K_{p2} C_w C_p}{(1 + K_a C_a + K_w C_w)^2} \quad (3.25)$$

$$r_e = \frac{k_2 K_a^2 C_a^2 - k_2^{-1} K_w K_e C_w C_e}{(1 + K_a C_a + K_w C_w)^2} = \frac{K_{e1} C_a^2 - K_{e2} C_w C_e}{(1 + K_a C_a + K_w C_w)^2} \quad (3.26)$$

E-R type:

$$r_p = \frac{k_1^{-1} K_a C_a - k_1 K_w C_w C_p}{1 + K_a C_a + K_w C_w} = \frac{K_{p1} C_a - K_{p2} C_w C_p}{1 + K_a C_a + K_w C_w} \quad (3.27)$$

$$r_e = \frac{k_2 K_a C_a^2 - k_2^{-1} K_w C_w C_e}{1 + K_a C_a + K_w C_w} = \frac{K_{e1} C_a^2 - K_{e2} C_w C_e}{1 + K_a C_a + K_w C_w} \quad (3.28)$$

with $K_{p1}=k_1^{-1}K_a$, $K_{p2}=k_1K_w$, $K_{e1}=k_2K_a$, $K_{e2}=k_2^{-1}K_w$ for E-R model and $K_{p1}=k_1^{-1}K_a$, $K_{p2}=k_1K_wK_p$, $K_{e1}=k_2K_a^2$, $K_{e2}=k_2^{-1}K_wK_e$ for L-H model.

The familiar power law model usually used for homogeneous reaction can be deduced from the L-H or E-R model for heterogeneous reaction by assuming that the adsorption is weak for all components. Assuming $1+K_pC_p+K_eC_e+K_aC_a+K_wC_w \approx 1$, the rate equations become:

$$r_p = K_{p1}C_a - K_{p2}C_w C_p = k_{11}(C_wC_p - C_a/K_{E1}) \quad (3.29)$$

$$r_e = K_{e1}C_a^2 - K_{e2}C_wC_e = k_{22}(C_a^2 - C_eC_w/K_{E2}) \quad (3.30)$$

3.4.3 Estimation of Parameters

Experimental reaction rate data was processed using a nonlinear regression method with the kinetic models described in Section 3.4.2. The sum of squares was the minimized variable and was calculated as the sum of the squares of the difference between the predicted and experimental values. For each reaction temperature, 25-34 data points were used to calculate the parameters. The standard difference between the predicted and experimental values was used to evaluate the quality of the model in relation to the prediction of the reaction rate. Simplified E-R model with surface reaction as rate-determining step (Equations 3.27 and 3.28) gave the best fit of the data (Table 3.2). The effect of temperature on reaction rate was modeled using the Arrhenius expression. The parameters of E-R model are:

$$K_{p1} = 1.297E30 * \exp(-31913/T) \quad (3.31)$$

$$K_{p2}=1.245E22*EXP (-24321/T) \quad (3.32)$$

$$K_a=8.310E-2*EXP (-1942/T) \quad (3.33)$$

$$K_w=3.539E-46*EXP (44554/T) \quad (3.34)$$

$$K_{e1}=6.360E-27*EXP (23886/T) \quad (3.35)$$

$$K_{e2}=5.481E-85*EXP (69989/T) \quad (3.36)$$

The kinetic model should not only be able to fit the experimental data, but it should be able to predict IPA conversion under different conditions. Additional kinetic runs were carried out at 418K. The kinetic parameter established using previous runs were used to predict the rate of IPA conversion at other initial concentration and temperature conditions. It can be seen from Figure 3.8 that E-R model is able to predict the IPA conversion well. The average stander error of the prediction is 8.4%.

3.5 Vapor-liquid Equilibria of Propylene-Water-IPA-DIPE System

The vapor-liquid equilibrium experimental results were compared with the prediction of the commercial simulation package Aspenlus™ to verify the prediction under the interested conditions. The built-in operation unit ‘Flush’ using UNIFAC method was used to calculate the vapor and liquid phase composition under the same conditions as those of equilibrium experiments. The predicted data has an average standard error of 7.3% with experimental results (Figure 3.9). It is therefore believed

that UNIFAC method is able to accurately predict the phase behavior of the propylene-water-IPA-DIPE system under the condition of interest (393-423K, 200-300psi).

3.6 Conclusions

The reaction kinetics for the hydration of propylene and etherification of IPA were studied using Amberlyst 38 as catalyst. The effects of stirring speed, temperature, catalyst loading and catalyst particle size on reaction rate were investigated. It was found that external mass transfer resistance to the reactions can be eliminated by increasing stirring speed beyond 800rpm. The internal mass transfer resistance is not significant under the test conditions. The kinetic reaction rate equations were developed using an Eley-Rideal model. The equations can be used in the design of catalytic distillation process for IPA production through propylene hydration.

3.7 Nomenclature

C	liquid phase concentration mole/l
$f_i^{*,l}$	liquid fugacity of pure component i at mixture temperature
V_i^G	partial mole volumes
k_1	propylene hydration rate constant
k_2	IPA etherification rate constant
k_1^{-1}	IPA dehydration rate constant
k_2^{-1}	DIPE decomposition rate constant
K	adsorption rate constant
L	mole number of liquid phase
M_i	molecular weight of component i
m_c	mass of catalyst gram
N	moles of compounds mole
N_{i0}	mole number of reactant i charged into batch reactor
r	reaction rate mole/min.g catalyst
t	reaction time minute
V	mole number of vapor phase
x_i	liquid phase mole fraction of component i
y_i	vapor phase mole fraction of component i
γ_i	liquid activity coefficient of component i

ϕ_i^v vapor phase fugacity coefficient of component i

θ_l fraction of vacant sites

θ_i fraction of active sites occupied by component i

Subscripts

a - IPA

e - DIPE

p - propylene

w - water

3.8 Literature Cited

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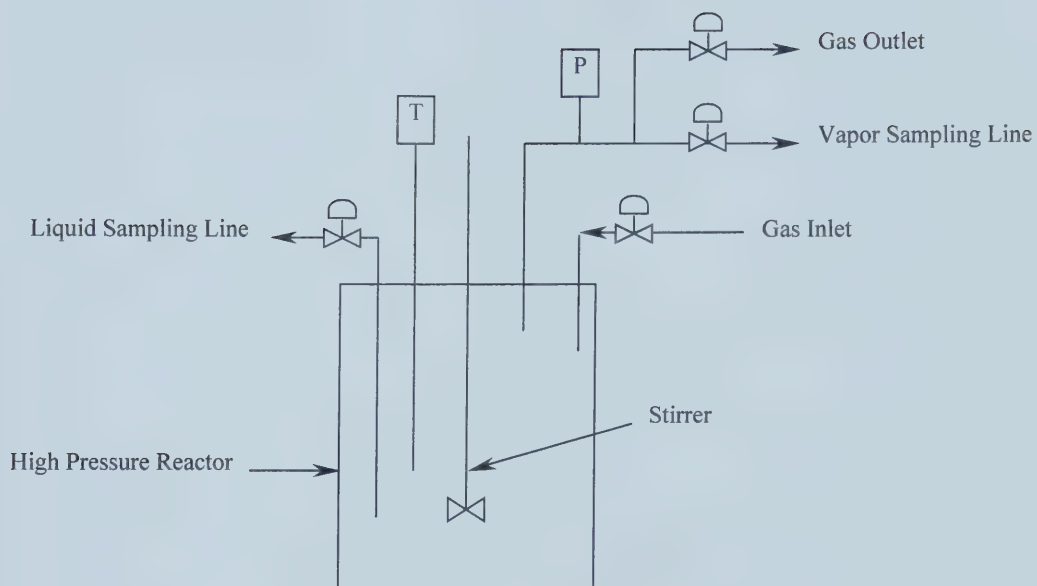


Figure 3.1 Batch slurry reaction system

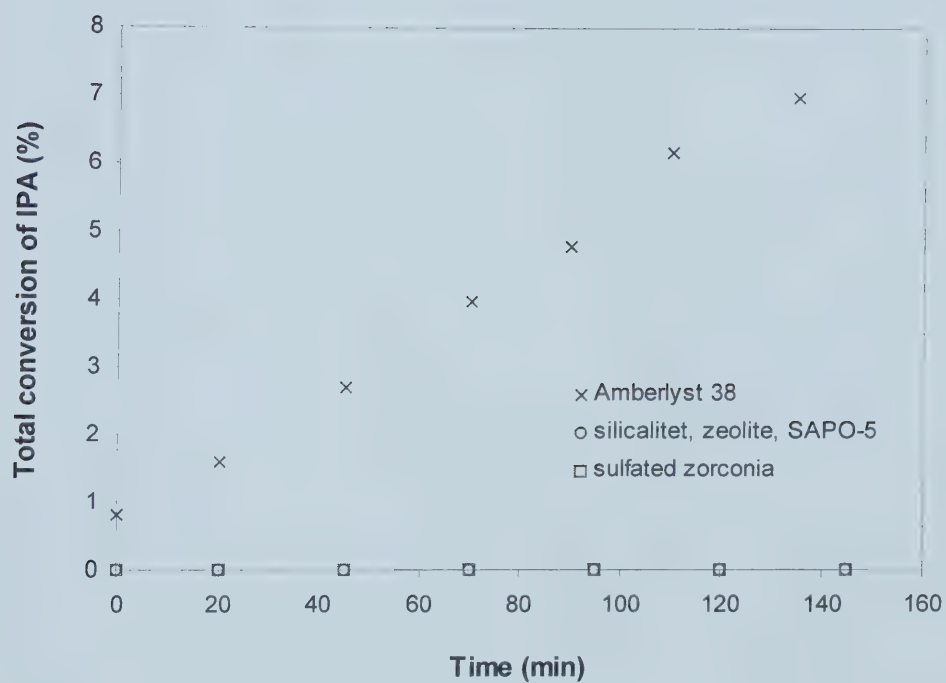


Figure 3.2 Catalyst screening

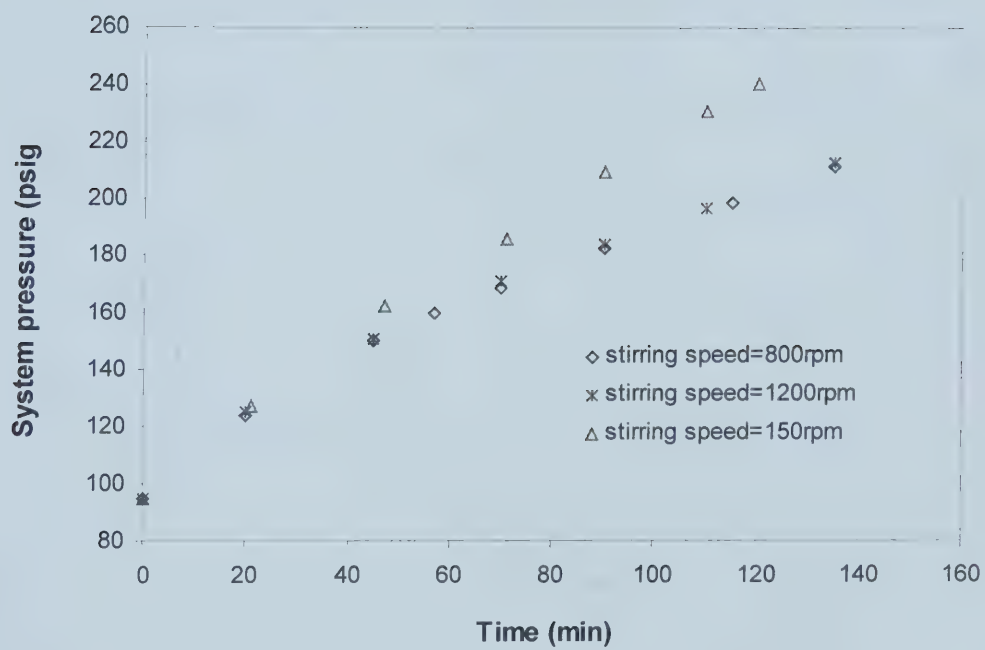


Figure 3.3 Effect of stirring speed

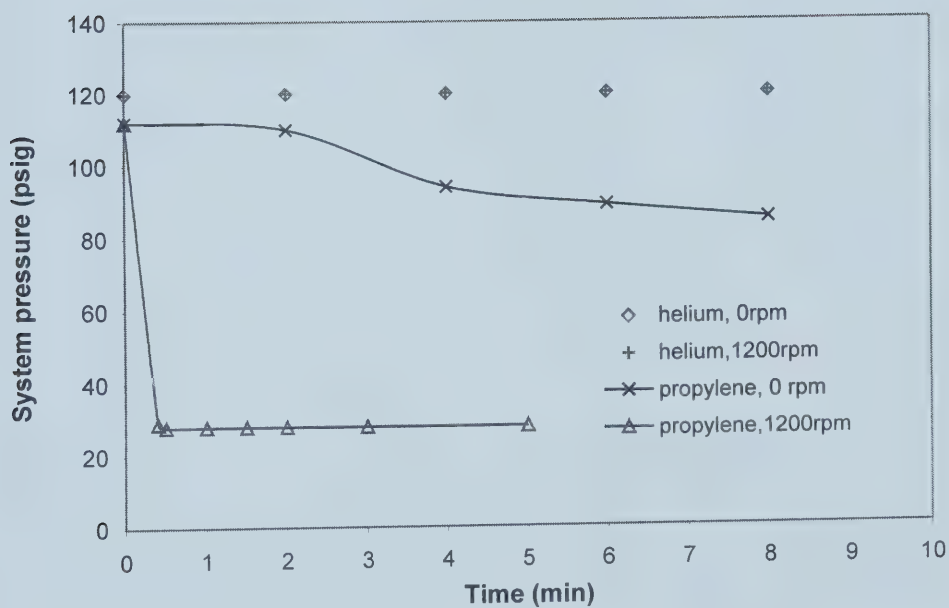


Figure 3.4 Effect of stirring speed on vapor liquid equilibrium

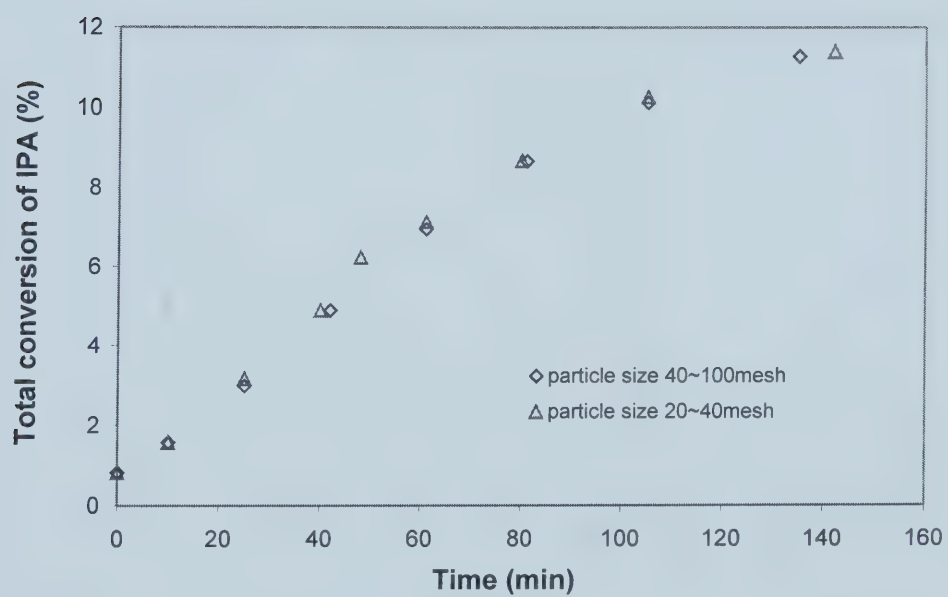


Figure 3.5 Effect of particle size on the overall reaction rate

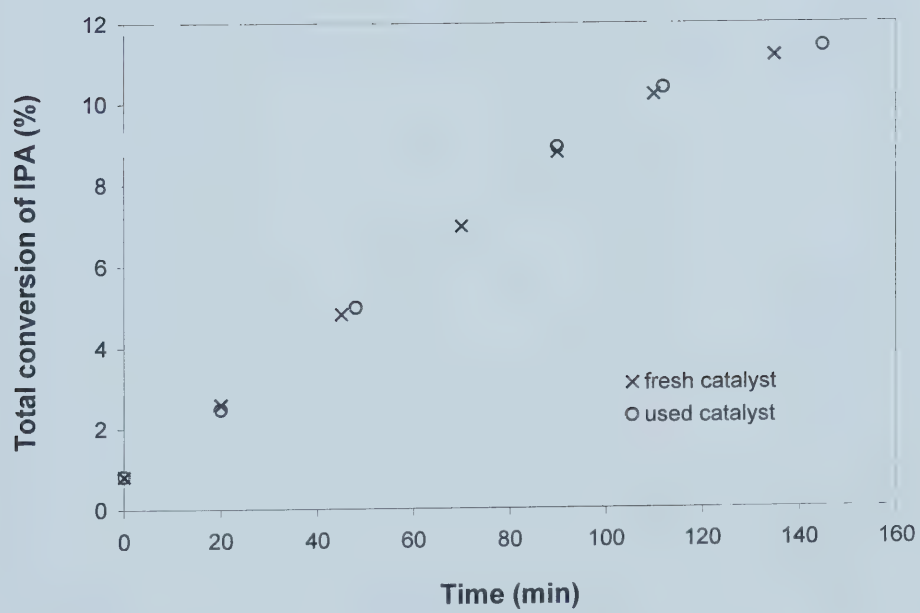


Figure 3.6 Catalyst reusability

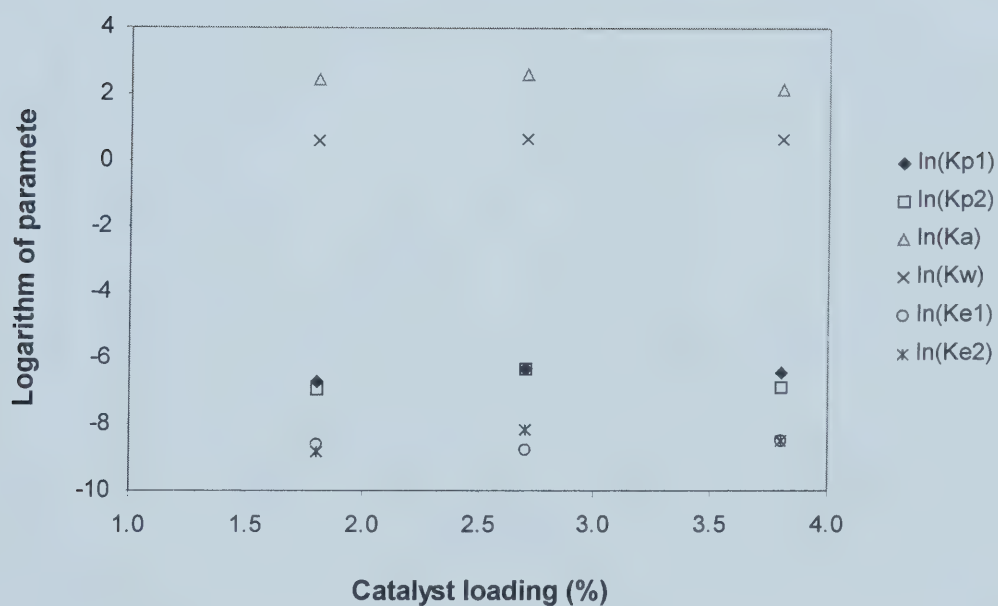


Figure 3.7 Effect of catalyst loading

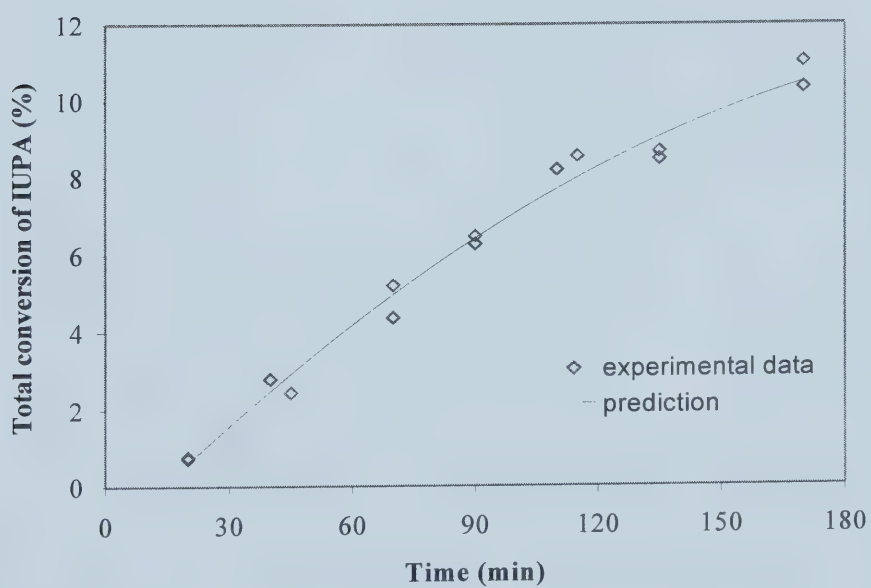


Figure 3.8 Comparison of experimental data with rate equation predicted conversion

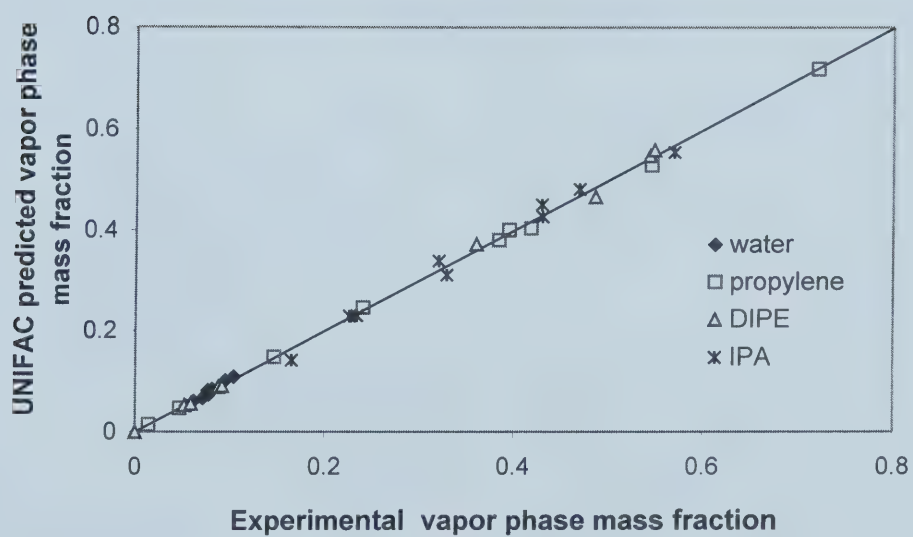


Figure 3.9 Comparison of experimental data with UNIFAC predicted data

Table 3.1 Property of Amberlyst 38

Physical form	opaque beads
Ionic form as shipped	hydrogen
Concentration of acid sites	>1.9eq/L; >5.3eq/Kg
Moisture holding capacity	51-57%
Shipping weight	810g/L
particle size	
Harmonic mean size	700-900um
Uniformity coefficient	<1.60
Finest content	<0.425mm: 1.9% max
Coarse beads	>1.180mm: 8.0%
Surface area	35m ² /g
Porosity	0.30ml/g
Average pore diameter	20nm
Temperature stability	up to 160 °C

Table 3.2 Comparison of kinetic models

Model type	rate-determining step	Standard error (%)
L-H	surface reaction	14.6
L-H	adsorption	19.8
E-R	surface reaction	8.1
E-R	adsorption	15.7
Power law		24.8

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusions

Catalytic distillation was applied to the production of IPA through propylene direct hydration. The optimum operating parameters for this catalytic distillation process were determined using a computer model. The simulation results show that the use of a catalytic distillation process overcomes chemical reaction equilibrium and vapor-liquid equilibrium limitations. The model shows that high purity IPA (up to 99.9 *mol%*) can be produced as a liquid product stream containing virtually no water. The reduction of water below the IPA-water azeotrope water content occurs by reaction of water with a 2.9:1 optimum molar excess of propylene when using a CD column having two spaced apart catalyst beds. Excess propylene is recycled to remove impurities that may otherwise accumulate in the CD column. The equilibrium ether content of the reaction mixture is retained in the reaction zones in the middle of the column therefore reduced the effect of side reaction. The optimum operation pressure is 2 MPa for the CD column, and the column temperature range is 323-460K, to allow simultaneous reaction and separation of the reaction mixture.

The reaction kinetics for the hydration of propylene and etherification of IPA were investigated using Amberlyst 38 as catalyst. The reactions were carried out in a batch

reactor. IPA, water and DIPE were used as initial reactants. Reaction rates were expressed as the formation rate of propylene and DIPE. The effects of stirring speed, temperature, catalyst loading and catalyst particle size on reaction rate were studied. L-H, E-R and power law mechanisms were proposed and screened. Eley-Rideal model was found to best describe the kinetic data.

4.2. Recommendations for Future Work

Future work should focus on design of a small-scale catalytic distillation column, laboratory experiments on the column, dynamic simulation and applications to industrial processes. A no-equilibrium model incorporating tray efficiency and kinetic equation would be able to predict the behavior of the CD process more accurately. A lab scale CD column should be designed and experimental data about the tray efficiency should be gathered.

Amberlyst 38 was used as propylene hydration catalyst, which is in the form of small beads. CD column internal should be carefully designed to ensure the high efficiency of catalyst beds.

The interaction between the chemical and phase equilibrium creates control problems not generally occur with conventional distillation. Tight process control may be required. Dynamic simulation of the process is needed to develop successful process control scheme.

APPENDIX

Input and Output Files for the Simulation of Catalytic Distillation Using Aspen Plus™

Input Summary created by Aspen Plus Rel. 10.1-0

IN-UNITS MET

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=200.

DATABANKS PURE10 / AQUEOUS / SOLIDS / INORGANIC / &
NOASPENPCD

PROP-SOURCES PURE10 / AQUEOUS / SOLIDS / INORGANIC

COMPONENTS

WATER H2O WATER /
PROPY-01 C3H6-2 PROPY-01 /
DIISO-01 C6H14O-3 DIISO-01 /
ISOPR-01 C3H8O-2 ISOPR-01 /
PROPA-01 C3H8 PROPA-01

FLOWSHEET

BLOCK B1 IN=PROFEED WATER WATER2 OUT=DISTILLA BUTTOM

PROPERTIES UNIFAC

PROPERTIES PRMHV2 / RKSMHV2

STREAM PROFEED

SUBSTREAM MIXED TEMP=298. <K> PRES=20. MOLE-FLOW=348.38
MOLE-FRAC PROPY-01 0.95 / PROPA-01 0.05

STREAM WATER

SUBSTREAM MIXED TEMP=298. <K> PRES=20. MOLE-FLOW=90.
MOLE-FRAC WATER 1.

STREAM WATER2

SUBSTREAM MIXED TEMP=298. <K> PRES=20. MOLE-FLOW=30.
MOLE-FRAC WATER 1.

BLOCK B1 RADFRAC

PARAM NSTAGE=30 ALGORITHM=NONIDEAL INIT-OPTION=STANDARD &
MAXOL=186 TOLOL=1E-005 FLASH-TOLIL=1E-005
COL-CONFIG CONDENSER=PARTIAL-V
FEEDS PROFEED 6 ON-STAGE / WATER 7 / WATER2 4
PRODUCTS DISTILLA 1 V / BUTTOM 30 L
P-SPEC 1 20. / 2 20.


```

COL-SPECS MOLE-D=231.4 MOLE-RR=33.
STAGE-EFF 1 0.7 / 2 0.7 / 3 0.7 / 4 0.7 / 5 0.7 / 6 0.7 / &
          7 0.7 / 8 0.7 / 9 0.7 / 10 0.7 / 11 0.7 / 12 &
          0.7 / 13 0.7 / 14 0.7 / 15 0.7 / 16 0.7 / 17 &
          0.7 / 18 0.7 / 19 0.7 / 20 0.7 / 21 0.7 / 22 &
          0.7 / 23 0.7 / 24 0.7 / 25 0.7 / 26 0.7 / 27 &
          0.7 / 28 0.7 / 29 0.7 / 30 0.7
REAC-STAGES 6 6 R-2 / 4 4 R-2
HOLD-UP 4 4 VOL-LHLDP=18.85.
HOLD-UP 6 6 VOL-LHLDP=48.87.
PROPERTIES UNIFAC
BLOCK-OPTION RESTART=NO
REPORT COMFBAL

STREAM-REPOR MOLEFLOW MASSFLOW STDVOLFLOW MOLEFRAC MASSFRAC &
          STDVOLFRAC

PROPERTY-REP PARAMS PCES PARAM-PLUS

REACTIONS R-2 REAC-DIST
          PARAM SUBROUTINE=RAT
          REAC-DATA 1 KINETIC
          REAC-DATA 2 KINETIC
          STOIC 1 ISOPR-01 -2. / DIISO-01 1. / WATER 1.
          STOIC 2 PROPY-01 -1. / WATER -1. / ISOPR-01 1.

SUBROUTINE RAT (N, NC, NRK, NRKV, NRKL,T, DUM1, DUM2,
               P, VF, F, X, Y, IDX, NBOPST, KDIAG,
               STOIC, IHLBAS, HLDLIQ, TIMLIQ, IHVBAS,
               HLDVP, TIMVAP, NINT, INT, NREAL, REAL,
               CRATE)

IMPLICIT REAL*8 (a-h, o-z)

DIMENSION X(NC), Y(NC), IND(NC), NBOPST(6), STOIC (NC,NRK),
          INT(NINT) REAL(NREAL), CRATE(NC)

X1=X(1)
X2=X(2)
X3=X(3)
X4=X(4)

RATE1=HLDLIQ*10**3*((1.297E30*EXP (-31913/T)*X(4)-1.245E22*EXP (-24321/T)*
&X(1)*X(2))/(1+8.310E-2*EXP (-1942/T)*X(4)+3.539E-46*EXP (44554/T)*X(1)))

RATE2=HLDLIQ***3*((6.360E-27EXP (23886/T)*X(4)*X(4)-5.481E-85EXP
(69989/T)*
&X(1)*X(3))/(1+8.310E-2*EXP (-1942/T)*X(4)+3.539E-46*EXP (44554/T)*X(1)))

CRATE(1)=RATE2-RATE1
CRATE(2)=RATE1

```



```

CRATE(3)=RATE2
CRATE(4)=RATE1-2*RATE2

```

```

RETURN
END

```

Output Summary created by Aspen Plus Rel. 10.1-0

BLOCK: B1 MODEL: RADFRAC

```

-----
INLETS   - PROFEED  STAGE   6
           WATER    STAGE   7
           WATER2   STAGE   4
OUTLETS  - DISTILLA STAGE   1
           BUTTOM   STAGE  30

```

PROPERTY OPTION SET: UNIFAC UNIFAC / REDLICH-KWONG

	*** MASS AND ENERGY BALANCE ***			
	IN	OUT	GENERATION	RELATIVE DIFF.
CONVENTIONAL COMPONENTS				
(KMOL/HR)				
WATER	120.000	1.44855	-118.551	0.355271E-15
PROPY-01	330.961	212.395	-118.566	-0.210397E-14
DIISO-01	0.	0.143470E-01	0.143470E-01	-0.376341E-10
ISOPR-01	0.	118.537	118.537	-0.443576E-14
PROPA-01	17.4190	17.4190	0.	-0.632264E-14
TOTAL BALANCE				
MOLE (KMOL/HR)	468.380	349.814	-118.566	-0.397460E-14
MASS (KG/HR)	16857.0	16857.0		-0.733768E-14
ENTHALPY (CAL/SEC)	-0.231549E+07	-0.198024E+07		-0.144785

```

*****
****  RESULTS  ****
*****

```

*** COMPONENT SPLIT FRACTIONS ***

	OUTLET STREAMS	
	DISTILLA	BUTTOM

COMPONENT:		
WATER	1.0000	.15229E-05
PROPY-01	1.0000	.79853E-12
DIISO-01	.97307	.26931E-01
ISOPR-01	.10401E-02	.99896
PROPA-01	1.0000	.31944E-12

*** SUMMARY OF KEY RESULTS ***

TOP STAGE TEMPERATURE	K	353.265
BOTTOM STAGE TEMPERATURE	K	489.721
TOP STAGE LIQUID FLOW	KMOL/HR	7,636.20
BOTTOM STAGE LIQUID FLOW	KMOL/HR	118.414
TOP STAGE VAPOR FLOW	KMOL/HR	231.400
BOTTOM STAGE VAPOR FLOW	KMOL/HR	4,149.12
MOLAR REFLUX RATIO		33.0000
MOLAR BOILUP RATIO		35.0391
CONDENSER DUTY (W/O SUBCOOL)	CAL/SEC	-4,994,970.
REBOILER DUTY	CAL/SEC	5,330,220.

**** MAXIMUM FINAL RELATIVE ERRORS ****

DEW POINT	0.18042E-04	STAGE= 15
BUBBLE POINT	0.21658E-04	STAGE= 15
COMPONENT MASS BALANCE	0.98998E-07	STAGE= 16 COMP=DIISO-01
ENERGY BALANCE	0.88650E-05	STAGE= 13

**** PROFILES ****

NOTE REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE FLOWS FROM THE STAGE EXCLUDING ANY SIDE PRODUCT. FOR THE FIRST STAGE, THE REPORTED VAPOR FLOW IS THE VAPOR DISTILLATE FLOW. FOR THE LAST STAGE, THE REPORTED LIQUID FLOW IS THE LIQUID BOTTOMS FLOW.

STAGE	TEMPERATURE K	PRESSURE ATM	ENTHALPY CAL/MOL		HEAT DUTY CAL/SEC
			LIQUID	VAPOR	
1	353.26	20.000	-328.16	2560.1	-.49950+07
2	355.63	20.000	-2561.0	2042.4	
3	372.45	20.000	-10842.	239.16	
4	408.99	20.000	-28139.	-7477.8	
5	415.57	20.000	-35852.	-13813.	
6	418.57	20.000	-44837.	-17606.	
7	441.75	20.000	-58291.	-38693.	
8	453.46	20.000	-64227.	-51841.	
9	460.31	20.000	-66806.	-58186.	
10	465.31	20.000	-67840.	-61155.	
11	469.21	20.000	-68113.	-62528.	
12	472.25	20.000	-67972.	-63036.	
13	475.03	20.000	-67570.	-62992.	
14	478.14	20.000	-67017.	-62579.	
15	481.56	20.000	-66444.	-61998.	
16	484.62	20.000	-65967.	-61462.	
17	486.82	20.000	-65636.	-61079.	
18	488.17	20.000	-65436.	-60846.	

19	488.92	20.000	-65324.	-60718.	
20	489.32	20.000	-65266.	-60650.	
21	489.52	20.000	-65236.	-60616.	
22	489.62	20.000	-65221.	-60598.	
23	489.67	20.000	-65213.	-60590.	
24	489.70	20.000	-65209.	-60585.	
25	489.71	20.000	-65207.	-60583.	
26	489.72	20.000	-65207.	-60582.	
27	489.72	20.000	-65206.	-60581.	
28	489.72	20.000	-65206.	-60581.	
29	489.72	20.000	-65206.	-60581.	
30	489.72	20.000	-65206.	-60581.	.53302+07

STAGE	FLOW RATE KMOL/HR		FEED RATE KMOL/HR			PRODUCT RATE KMOL/HR	
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	7636.	231.4					231.4000
2	6614.	7868.					
3	6036.	6845.					
4	2313.	6267.	30.0000				
5	2005.	3220.					
6	3201.	2911.			348.3800		
7	3220.	3173.	90.0000				
8	3314.	3102.					
9	3481.	3196.					
10	3672.	3362.					
11	3830.	3553.					
12	3906.	3712.					
13	3906.	3788.					
14	3899.	3788.					
15	3941.	3781.					
16	4026.	3823.					
17	4114.	3907.					
18	4180.	3995.					
19	4221.	4061.					
20	4243.	4102.					
21	4255.	4125.					
22	4262.	4137.					
23	4265.	4143.					
24	4266.	4146.					
25	4267.	4148.					
26	4267.	4148.					
27	4267.	4149.					
28	4267.	4149.					
29	4268.	4149.					
30	118.4	4149.				118.4142	

		****	MOLE-X-PROFILE	****	
STAGE	WATER	PROPY-01	DIISO-01	ISOPR-01	PROPA-01

1	0.12567E-01	0.90909	0.82785E-03	0.23626E-02	0.75157E-01
2	0.27286E-01	0.87914	0.10452E-01	0.11352E-01	0.71774E-01
3	0.46989E-01	0.76727	0.84477E-01	0.41472E-01	0.59788E-01
4	0.30300E-01	0.56334	0.30702	0.55061E-01	0.44277E-01
5	0.89514E-01	0.46733	0.32454	0.94361E-01	0.24253E-01
6	0.23214	0.33518	0.20699	0.21527	0.10432E-01
7	0.26407	0.14954	0.27329	0.30906	0.40468E-02
8	0.22021	0.67166E-01	0.30971	0.40130	0.16177E-02
9	0.15632	0.30651E-01	0.32803	0.48432	0.67851E-03
10	0.98225E-01	0.14125E-01	0.33108	0.55627	0.29641E-03
11	0.56925E-01	0.64233E-02	0.31506	0.62146	0.13086E-03
12	0.31551E-01	0.27990E-02	0.27655	0.68904	0.56293E-04
13	0.17002E-01	0.11343E-02	0.21784	0.76400	0.22804E-04
14	0.88420E-02	0.41973E-03	0.15121	0.83952	0.85232E-05
15	0.43805E-02	0.14236E-03	0.93172E-01	0.90230	0.29449E-05
16	0.20679E-02	0.45202E-04	0.52472E-01	0.94541	0.95820E-06
17	0.94147E-03	0.13760E-04	0.27904E-01	0.97114	0.29995E-06
18	0.41904E-03	0.40887E-05	0.14362E-01	0.98522	0.91829E-07
19	0.18417E-03	0.11993E-05	0.72635E-02	0.99255	0.27778E-07
20	0.80404E-04	0.34942E-06	0.36405E-02	0.99628	0.83507E-08
21	0.34983E-04	0.10146E-06	0.18163E-02	0.99815	0.25025E-08
22	0.15195E-04	0.29410E-07	0.90409E-03	0.99908	0.74872E-09
23	0.65942E-05	0.85176E-08	0.44949E-03	0.99954	0.22383E-09
24	0.28604E-05	0.24658E-08	0.22332E-03	0.99977	0.66890E-10
25	0.12404E-05	0.71368E-09	0.11090E-03	0.99989	0.19985E-10
26	0.53768E-06	0.20653E-09	0.55038E-04	0.99994	0.59700E-11
27	0.23294E-06	0.59757E-10	0.27288E-04	0.99997	0.17831E-11
28	0.10078E-06	0.17281E-10	0.13506E-04	0.99999	0.53226E-12
29	0.43479E-07	0.49893E-11	0.66616E-05	0.99999	0.15861E-12
30	0.18630E-07	0.14323E-11	0.32629E-05	1.0000	0.46991E-13

**** MOLE-Y-PROFILE ****

STAGE	WATER	PROPY-01	DIISO-01	ISOPR-01	PROPA-01
1	0.62599E-02	0.91787	0.60331E-04	0.53280E-03	0.75277E-01
2	0.12381E-01	0.90934	0.80528E-03	0.23088E-02	0.75161E-01
3	0.26576E-01	0.88045	0.10101E-01	0.10986E-01	0.71892E-01
4	0.45486E-01	0.77283	0.81360E-01	0.39960E-01	0.60360E-01
5	0.11352	0.68967	0.10226	0.57324E-01	0.37223E-01
6	0.16311	0.63695	0.92622E-01	0.84628E-01	0.22686E-01
7	0.26258	0.33818	0.20884	0.17988	0.10525E-01
8	0.27415	0.15525	0.28372	0.28269	0.42013E-02
9	0.22837	0.69654E-01	0.32118	0.37912	0.16777E-02
10	0.16182	0.31730E-01	0.33958	0.46616	0.70240E-03
11	0.10150	0.14595E-01	0.34211	0.54149	0.30629E-03
12	0.58741E-01	0.66282E-02	0.32511	0.60939	0.13504E-03
13	0.32537E-01	0.28865E-02	0.28520	0.67932	0.58053E-04
14	0.17533E-01	0.11698E-02	0.22465	0.75662	0.23516E-04
15	0.91189E-02	0.43287E-03	0.15594	0.83450	0.87901E-05
16	0.45162E-02	0.14677E-03	0.96058E-01	0.89928	0.30362E-05
17	0.21306E-02	0.46572E-04	0.54063E-01	0.94376	0.98724E-06
18	0.96937E-03	0.14168E-04	0.28731E-01	0.97028	0.30884E-06

19	0.43126E-03	0.42079E-05	0.14780E-01	0.98478	0.94507E-07
20	0.18948E-03	0.12339E-05	0.74731E-02	0.99234	0.28580E-07
21	0.82712E-04	0.35945E-06	0.37449E-02	0.99617	0.85904E-08
22	0.35984E-04	0.10436E-06	0.18682E-02	0.99810	0.25741E-08
23	0.15629E-04	0.30250E-07	0.92984E-03	0.99905	0.77012E-09
24	0.67820E-05	0.87608E-08	0.46223E-03	0.99953	0.23023E-09
25	0.29415E-05	0.25362E-08	0.22961E-03	0.99977	0.68798E-10
26	0.12752E-05	0.73401E-09	0.11397E-03	0.99988	0.20554E-10
27	0.55249E-06	0.21239E-09	0.56515E-04	0.99994	0.61391E-11
28	0.23905E-06	0.61422E-10	0.27973E-04	0.99997	0.18326E-11
29	0.10313E-06	0.17734E-10	0.13798E-04	0.99999	0.54611E-12
30	0.44188E-07	0.50908E-11	0.67586E-05	0.99999	0.16180E-12

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